PRACTICAL RUBBER COMPOUNDING AND PROCESSING

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COLIN W. EVANS
F.P.R.I., F.I.R.I., A.R.T.C.S., F.Inst.Pet.

Formerly Technical Director, Dunlop Limited,
Gateshead-on-Tyne, England
Chairman, Hose Technical Committees of the
International Standards Organisation and the
British Standards Institution

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To my wife, Dot
and sons, Barry and Steve

PREFACE

An attempt has been made in this book to simplify the many facets of rubber compounding and processing plant in use throughout the world. The emphasis throughout is of a practical nature and on problems encountered in the day-to-day running of a typical rubber factory.

Scientific explanations and descriptions have, however, been included, but only where essential for understanding; no attempt has been made to enter into wider theoretical aspects. There are already many excellent works in this field, and these should be referred to if further information is required. In addition, all the major chemical and rubber suppliers to the industry will be only too pleased to assist if requested.

I would like to thank my company and colleagues for their help and advice, and also my secretaries Mrs Helen Fielding and Mrs Leslie Maddison for their invaluable assistance; also the plant and machinery manufacturers who have supplied photographs (acknowledgement is made in the text). Gratitude is also expressed to my many friends within the ISO, BSI, and the British and American Rubber Manufacturers Associations. In addition, I am also grateful to them for permission to use information.

In conclusion, I would especially thank my wife for her usual encouragement, good humour and understanding, during the long months of the book's preparation.

COLIN W. EVANS
Low Fell
Gateshead

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CHAPTER 1

POLYMERS AND RAW MATERIALS

Rubber compounding as we know it today is the result of the considerable work, effort, and contributions of countless workers in this field, since the discovery of vulcanisation in 1839. It covers almost a century and a half of applied research and development, and the healthy state of this science and the rubber industry today, is in no small measure due to this.

Today's compounder or rubber chemist must be competent in the use and application of both natural and synthetic materials, and, to do this to best advantage, requires the following:

(1) An understanding of the plant and processing methods available.
(2) A thorough knowledge of both the chemical and physical properties of the raw materials available.
(3) A knowledge of these materials and their modifications contributing to satisfactory service life of the compound and the final product.
(4) A knowledge of the vulcanising systems available in order to bring out, develop and maximise the ultimate properties of the materials used.
(5) An understanding of the in-process and final testing of the finished products, so as to ensure consistency.
(6) Last, but by no means least, the capability of producing material that will process well in the factory, and at the right price to be commercially viable.

The polymers and elastomers listed in Table 1 are widely used in everyday and specialised rubber goods manufacture. For ease and convenience they are shown also with their general properties and characteristics.

TABLE I

POLYMERS AND ELASTOMERS USED IN RUBBER MANUFACTURE

International designation	*Common name*	*Chemical composition*	*General properties*
ABR	Acrylic	Acrylate–Butadiene	Excellent high temperature oil and air. Poor cold flow and low temperature. Not recommended for water service.
AFMU	Fluon Teflon PTFE	Tetrafluoroethylene	Excellent and outstanding high temperature and chemical resistance.
AU	Urethane	Polyester	Excellent ageing, abrasion, tear and solvent resisting properties. Poor high temperature characteristics.
BIIR	Brominated butyl	Bromo-isobutene–Isoprene	Excellent ageing, and weathering resistance with good physical properties. Low permeability to air. Very poor resistance to petroleum based fluids.
BR	Butadiene rubber	Butadiene	Excellent low temperature and abrasion properties, with high resilience.
CIIR	Chlorinated butyl	Chloro-isobutene–Isoprene	As for BIIR.
CM	Chlorinated Polyethylene	Chloropolyethylene	Excellent UV, weathering, oil, chemical and flame resistance. Good low temperature impact resistance.

CO	Hydrin	Polychloromethyl oxirane	Excellent ozone and oil resistance, with low permeability to gases. Good flame resistance, with moderate low temperature properties.
CR	Neoprene	Chloroprene	Good ageing and weathering resistance with good physical properties. Fair resistance to petroleum based fluids, but not high aromatics. Flame retarding.
CSM	Hypalon	Chlorosulphonyl-polyethylene	Excellent weathering, ozone, and acid resistance. Reasonable resistance to petroleum based fluids but not aromatics.
ECO	Hydrin	Ethylene oxide and chloromethyl oxirane	Excellent ozone and oil resistance. Good low temperature properties. Reasonable flame resistance; with low gas permeability.
EPDM	Ethylene propylene rubber	Ethylene propylene diene terpolymer	Excellent resistance to weathering, ozone, heat, water, steam, glycolether brake fluids and vegetable oils. Poor resistance to petroleum based fluids, including mineral oils,
EPM	Ethylene propylene rubber	Ethylene propylene	
EPR	Ethylene propylene rubber	Ethylene propylene	

(continued)

TABLE 1—*contd.*

International designation	*Common name*	*Chemical composition*	*General properties*
EPT	Ethylene propylene rubber	Ethylene propylene terpolymer	
EU	Urethane	Polyether	Excellent ageing, abrasion, tear and solvent resisting properties. Poor high temperature characteristics.
FMQ	Fluorosilicone	Trifluoropropyl siloxane	Excellent mineral oil fuel resistance. Other properties as VMQ.
FPM	Viton fluorocarbon	Hexafluoropropylene·vinylidene fluoride	Excellent high temperature resistance with air and oil. Excellent chemical resistance.
IR	Polyisoprene	Isoprene, synthetic	As for natural rubber.
IIR	Butyl	Iso-butene isoprene	As for BIIR.
NR	Natural	Isoprene, natural	Excellent physical properties including abrasion, and low temperature resistance. Poor resistance to petroleum based fluids.
NBR	Nitrile Buna N	Nitrile butadiene	Excellent resistance to petroleum based fluids with good physical properties. Reasonably resistant to aromatics.
PA	Nylon	Polyamide	Good abrasion, chemical, high temperature and fatigue resistance. Low gas permeation, and a very low coefficient of friction.

PE	Polythene Polyethylene	Ethylene	Excellent dielectric, water, acid, alkali and chemical resistance.
PP	Polypropylene	Propylene	
PTFE	See AFMU		
PVC	Polyvinyl chloride	Vinyl chloride	Good weather resistance, flame resistance. Poor low and high temperature properties.
SBR	SBR (Originally known as GRS)	Styrene–Butadiene	Good physical properties, including abrasion, but has poor resistance to petroleum based fluids.
T	Thiokol	Organic polysulphide	Exceptional solvent and weather resistance. Most other properties, poor.
—	Thermoplastic rubber	Polyolefins Blocked co-polymers of styrene and butadiene	Good weather and chemical resistance between −50 °C and +120 °C.
VMQ	Silicone	Dimethyl polysiloxane	Excellent high and low temperature resistance, with reasonable physical properties.
XPLE	Cross-linked polyethylene	Polyethylene with cross-linking agent	Excellent chemical, heat and electrical properties.

CARBON BLACK

Perhaps at first glance, the lists of the various carbon blacks available to the rubber compounder is rather confusing and frightening. It could even be argued that there are far too many types available, and that some rationalisation is long overdue. The carbon black producers would be the first to agree with this, and indeed attempts are currently being made in this direction by them. Unfortunately, in the past, to give the industry and the user what industry *believes* it requires, the carbon black producers have been over co-operative. Subsequently, because of this the present proliferation has occurred.

However, the following historical background into the available types of carbon black will be of interest (Courtesy: Cabot Carbon and Ashland Chemicals) and it is trusted will help clarify the situation somewhat.

Classification of Carbon Blacks

The former 'industry letter' classification system of carbon black grades for rubber, which is still used, is confusing and even ludicrous. As each new grade was introduced, its sponsor gave it a designation different from prevailing grades and descriptive of its distinguishing characteristics. Thus, we have classification in accordance with levels of abrasion resistance—high abrasion furnace (HAF), intermediate super abrasion furnace (ISAF), and super abrasion furnace (SAF); classification in accordance to reinforcement—semi-reinforcing furnace (SRF); classification based on vulcanisate property—high modulus furnace (HMF); classification based on a rubber processing property—fast extrusion furnace (FEF); classification based on usefulness—general purpose furnace (GPF) and all-purpose (APF); classification based on 'particle' size—fine furnace (FF), and large particle size furnace (LPF); and a classification based on electrical conductive properties (XCF). Within some of these broad grades there are a variety of subgrades having different 'structure' levels, an example being HAP, with a high structure subgrade (HAF-HS) and a low structure subgrade (HAF-LS). Other features have been used to designate various subgrades. The obvious inadequacies of this unwieldy classification procedure led the ASTM Committee D-24 on carbon black to establish a letter and number system, illustrated in Table 2. In the ASTM system the N-series numbers increase as iodine adsorption values or surface areas decrease. The SAF grades have designated numbers from N100–N199; the ISAF grades, N200–

TABLE 2
CARBON BLACK—ASTM GRADE NUMBERS

Blacks	*Iodine adsorption range*
N1	140 maximum
N2	100–139
N3	75–99
N4	55–74
N5	41–54
N6	32–40
N7	20–31
N8	15–19
N9	Below 15

N299; the HAF grades, N300–N399; the HMF, GPF, and APF grades, N600–N699; the SRF grades, N700–N799; fine thermal (FT) has been designated as N880, and medium thermal (MT) N990. Quality variations, such as differences in structure, are given arbitrary numbers within a grade. Table 3 lists a selected group of carbon black grades, their ASTM number, their type category and some important typical analytical properties.

A first glance at Table 3 leads one to question the need for so many ASTM grade numbers, some of them being rather close in distinguishing properties. The answer is that iodine adsorption and DBP do not in themselves classify adequately carbon black performance. Thus, improvements or changes in process technology may provide a product with similar values of iodine adsorption and DBP value to an existing grade but with performance features different enough to require a new number. The finest particle size grade is designated by the N100 series of numbers and the numbers increase with increasing 'particle' size or decreasing surface area to the largest particle size grades which are the N900 series. A new grade may be introduced to fill a gap in the quality range, to satisfy a customer need or to provide a lower cost product. It is obvious that these discrete particles have resulted in such a proliferation of grades that rubber compounders find them difficult to understand and expensive to evaluate and stock. Also, the larger number of grades increases manufacturing, storage and distribution costs. In recent years there has been an effort on the part of both suppliers and customers to rationalise the carbon black grade dilemma. It will be seen that as well as black numbers being in an N-series, there are a few blacks with the prefix 'S'. The prefix 'N' stands for normal cure and 'S'

TABLE 3
TYPICAL ANALYTICAL PROPERTIES OF RUBBER GRADE CARBON BLACKS

Nomenclature *ASTM*[a]	*Type*	*Typical iodine adsorption Number D1510*[b]	*Typical DBP Number D2414*	*Typical pour density, kg/m³ (lb/ft³) D1513*	*Tinting strength*[c] *IRB no. 3 (%)*
N110	SAF	145	113	335 (21·0)	128
N121	SAF–HS	120	130	320 (20·0)	
N166		150	135	320 (20·0)	122
S212		117	86	400 (25·0)	—
N219	ISAF–LS	118	78	440 (27·5)	124
N220	ISAF	121	114	345 (21·5)	114
N231	ISAF–LM	125	91	390 (24·5)	117
N234		118	125	320 (20·0)	130
N242	ISAF–HS	123	126	330 (20·5)	119
N270		102	124	345 (21·5)	—
N285		102	126	335 (21·0)	104
N293	CF	145	100	375 (23·5)	119
N294	SCF	205	106	370 (23·0)	119
S300		105	102	350 (22·0)	—
S301		115	99	350 (22·0)	—
S315		86	79	450 (28·0)	—
N326	HAF–LS	82	71	465 (29·0)	109
N327		86	60	510 (32·0)	120
N330	HAF	82	102	375 (23·5)	104
N332		84	102	375 (23·5)	118
N339	HAF–HS	90	120	345 (21·5)	114
N347	HAF–HS	90	124	335 (21·0)	104
N351		67	120	345 (21·5)	100
N356		93	150	305 (19·0)	103
N358	SPF	84	150	290 (18·0)	99
N363		66	68	480 (30·0)	110
N375	HAF	90	114	360 (22·5)	116
N440	FF	50	60	480 (30·0)	—
N472	XCF	270	178	255 (16·0)	
N539		42	109	385 (24·0)	—
N542		44	67	505 (31·5)	
N550	FEF	43	121	360 (22·5)	—
N568	FEF–HS	45	132	335 (21·0)	—
N601		35	84	425 (26·5)	—
N650	GPF–HS	36	125	370 (23)	—
N660	GPF	36	91	425 (26·5)	—
N683	APF	30	132	335 (21·0)	—
N741		20	105	370 (23·0)	—
N754		25	58	495 (31·0)	—
N762	SRF–LM	26	62	505 (31·5)	—
N765	SRF–HS	31	111	375 (23·5)	—
N774	SRF–HM	27	70	495 (31·0)	—

TABLE 3—*contd.*

Nomenclature *ASTM*[a]	*Type*	*Typical iodine adsorption Number D1510*[b]	*Typical DBP Number D2414*	*Typical pour density, kg/m*^{3} *(lb/ft*^{3}*) D1513*	*Tinting strength*[c] *IRB no. 3 (%)*
N785		25	126	335 (21·0)	—
N787		31	81	450 (28·0)	—
N880	FT	13	35	605 (38·0)	—
N881	FT	13	35	605 (38·0)	—
N907	MT	7	33	655 (41·0)	—
N908	MT	7	33	655 (41·0)	—
N990	MT	7	33	655 (41·0)	—
N991	MT	7	33	655 (41·0)	—

[a] ASTM designations are determined according to Recommended Practice D2516, Nomenclature for Rubber-Grade Carbon Blacks.

[b] In general, Method D1510 can be used to estimate the surface area of furnace blacks but not channel, oxidised, or thermal blacks.

[c] Industry reference HAF black taken as 100.

indicates a slow curing black. At one time, the slow blacks were chemical blacks, but these are no longer available and any 'S' black is now an oxidised furnace one. In the 'N' series the numbers increase as iodine adsorption values decrease, but no range of values are as yet specified. This is under very active consideration within the carbon black committee of ISO TC45 and will very shortly be specified. The suggested ranges are shown in Table 2.

Properties of Carbon Black/Rubber Compounds

The general effects of carbon black on rubber properties are similar in all rubbers, being dominated mainly by surface area, 'particle' size and 'structure' level or aggregate size. High surface area, small 'particle' size carbon blacks impart higher levels of reinforcement as reflected in tensile strength and resistance to abrasion and tearing. Higher hysteresis and poorer dynamic performance are the price paid for these improvements. Higher 'structure' or aggregate size gives improved extrusion behaviour, higher stock viscosities, improved 'green' strength and higher modulus values. A summary of the effects of carbon black 'structure' and 'particle' size on rubber processing and vulcanisate properties is listed in Table 4.

TABLE 4

APPLICATIONS OF MAJOR RUBBER GRADE CARBON BLACKS

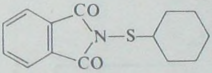
ASTM N-Type	*Designation*	*General rubber properties*	*Typical uses*
N990	Medium thermal (MT)	Low reinforcement, modulus, hardness, hysteresis, tensile strength; high loading capacity and high elongation	Wire insulation and jackets, mechanical goods, footwear, belts, hose, packings, gaskets, O-rings, mountings, tyre innerliners
N880	Fine thermal (FT)	Low reinforcement, modulus, hardness, hysteresis, tensile strength; high elongation, tear strength, and flex resistance	Mechanical goods, gloves, bladders, tubes, footwear uppers
N700 Series	Semi-reinforcing (SRF)	Medium reinforcement, high elongation, high resilience, low compression set	Mechanical goods, footwear, inner tubes, floor mats, hose
N660	General purpose (GPF)	Medium reinforcement, medium modulus, good flex and fatigue resistance, low heat build-up	Standard tyre carcass black; tyre innerliners and widewalls; sealing rings, cable jackets, hose, soling, and extruded goods; EPDM compounds
N650	General purpose-high structure (GPF–HS)	Medium reinforcement, high modulus and hardness, low die swell, smooth extrusion	Tyre innerliners, carcass, radial belt and sidewall compounds; extruded goods and hose
N550	Fast extrusion (FEF)	Medium-high reinforcement; high modulus and hardness; low die swell and smooth extrusion	Tyre innerliners, carcass, and sidewall compounds; innertubes, hose and extruded goods
N326	High abrasion-low structure (HAF–LS)	Medium-high reinforcement; low modulus, high elongation, good fatigue resistance, flex resistance, and tear strength	Tyre belt, carcass, and sidewall compounds
N330	High abrasion (HAF)	Medium-high reinforcement; moderate modulus, good processing	Tyre belt, sidewall, and carcass compounds; retread compounds, mechanical and extruded goods
N339, N347, N375	High abrasion-high structure (HAF–HS)	High reinforcement, modulus, and hardness; excellent processing	Standard tyre tread blacks
N220	Intermediate super abrasion (ISAF)	High reinforcement, tear resistance; good processing	Passenger and off-the-road tyre treads; special service tyres
N110	Super abrasion (SAF)	High reinforcement	Special tyre treads, airplane, off-the-road, racing tyres; products for highly abrasive service

Rubber property changes produced by carbon black addition depend on the loading level. Reinforcement increases with increased loading to an optimum, and then decreases. The optimum is normally in the range of 40 to 60 parts per hundred of the rubber phase, usually composed of a combination of rubber polymer and softening oil. Increasing the loading level from 35 to 80 parts per hundred produces more or less linear increases in hardness and modulus. The magnitude of these changes increases with 'structure' and the specific gravity of the rubber phase (elastomer plus oil).

ANTIOXIDANTS/ACCELERATORS

Tables 5 and 6 list the most widely used materials in the above classifications. Other major ingredients used in the rubber industry are discussed in Chapter 2.

Retarders

Chemical name	*N*-(cyclohexyl thio)phthalimide
Chemical formula	
Specific gravity	1·25/1·35
Melting point	90 °C
Supplier	Monsanto

Blowing Agents

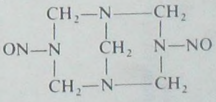
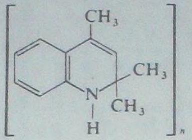
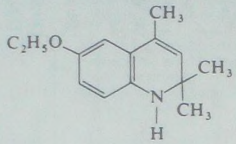
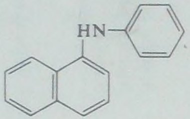
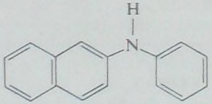
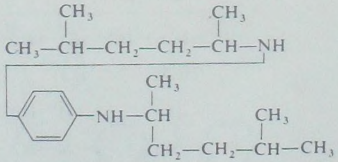
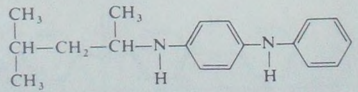
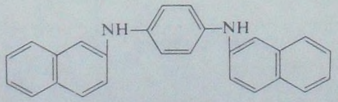
Chemical name	Dinitroso-pentamethylenetetramine (DNPT)
Chemical formula	
Specific gravity	1·4
Melting point	120 °C—decomposes
Normal usage levels	1–5 phr
Safety handling code	B
Suppliers	Bayer Vulnax DuPont

TABLE 5
ANTIOXIDANTS/ANTIDEGRADANTS

Chemical name	*Formula*	*Specific gravity*	*Melting point*	*Supplier*
Acetone-diphenylamine condensate ADPA	Complex	1·1	Viscous liquid	Anchor Uniroyal Vulnax
Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline TQ		1·1	80 °C	Anchor Monsanto Vulnax Bayer
6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline ETMQ		1·0	Viscous liquid BP 125 °C	Monsanto Bayer
Phenyl-α-naphthylamine PAN		1·2	54 °C	Bayer

Phenyl-*β*-naphthylamine PBN		1·2	106 °C	Anchor Bayer
Octylated diphenylamine ODPA	Complex	1·0	95 °C	Vulnax Uniroyal
N,*N*′-bis(1,4-dimethyl-pentyl)-*p*-phenylenediamine 77PD		0·9	Liquid BP 184 °C	Uniroyal Monsanto Universal Oil-Products Bayer
N-1,3-dimethylbutyl-*N*′-phenyl-*p*-phenylenediamine 6PPD		1·0	40/50 °C	Monsanto Vulnax Uniroyal Universal Oil-Products Bayer
N,*N*′-di-*β*-naphthyl-*p*-phenylenediamine DNPD		1·3	230 °C (approximately)	Anchor

(continued)

TABLE 5—*contd.*

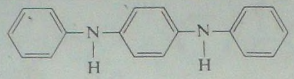
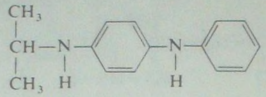
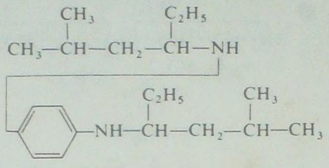
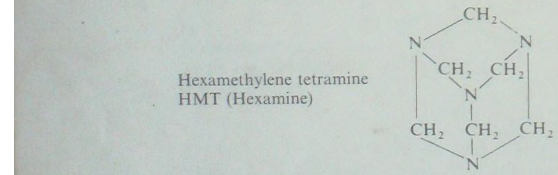
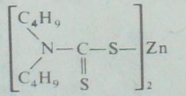
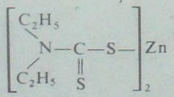
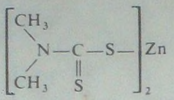
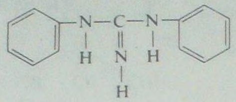
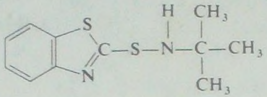
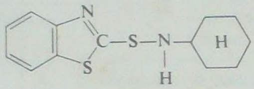
Chemical name	*Formula*	*Specific gravity*	*Melting point*	*Supplier*
N,N'-diphenyl-*p*-phenylenediamine DPPD		1·3	130 °C	Vulnax Anchor Uniroyal
N-isopropyl-*N'*-phenyl-*p*-phenylenediamine IPPD		1·1	73 °C (approximately)	Anchor Uniroyal Monsanto Vulnax Bayer
N,N'-bis(1-ethyl-3-methylpentyl)-*p*-phenylenediamine DOPD		0·9	Liquid BP 100 °C	Universal Oil-Products Uniroyal
Mixed diaryl-*p*-phenylenediamine Wingstay 100	Complex	1·2	87/97 °C	Goodyear

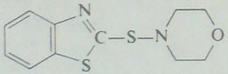
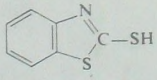
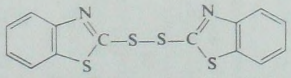
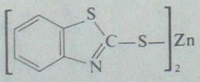
TABLE 6
VULCANISING AGENTS—ACCELERATORS

Chemical name	*Formula*	*Specific gravity*	*Melting point*	*Supplier*
Butyraldehyde-aniline	Complex	0·95	—	Uniroyal
Hexamethylene tetramine HMT (Hexamine)		1·3	Sublimes 260 °C	Bayer
Zinc dibutyl dithiocarbamate ZDBC	 $\left[(C_4H_9)_2N{-}C({=}S){-}S{-}\right]_2Zn$	1·25	108 °C	Anchor Uniroyal Robinson Vulnax
Zinc diethyl dithiocarbamate ZDEC	 $\left[(C_2H_5)_2N{-}C({=}S){-}S{-}\right]_2Zn$	1·47	178 °C	Anchor Ugine Kuhlmann Monsanto Uniroyal Robinson Vulnax Bayer

(continued)

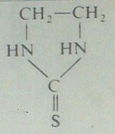
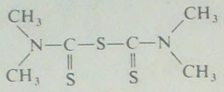
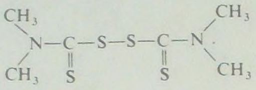
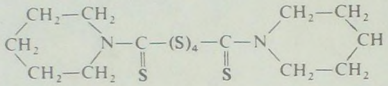
TABLE 6—*contd.*

Chemical name	*Formula*	*Specific gravity*	*Melting point*	*Supplier*
Zinc dimethyl dithiocarbamate ZDMC		1·65	245 °C	Anchor DuPont Monsanto Uniroyal Robinson Vulnax Bayer
Diphenylguanidine DPG		1·19	145 °C	Anchor Monsanto Ugine Kuhlmann Vulnax Bayer
N-tert-butyl-2-benzthiazl sulphenamide TBBS		1·30	105 °C	Monsanto Uniroyal Bayer
N-cyclohexyl-2-benzthiazyl sulphenamide CBS		1·30	100 °C	Anchor Uniroyal Ugine Kuhlmann Monsanto Vulnax Bayer

2-(morpholinothio benzothiazole) MBS		1·35	80 °C	Uniroyal Anchor Monsanto Vulnax Bayer
2-mercapto benzothiazole MBT		1·49	177 °C	Anchor Vanderbilt Monsanto Vulnax Bayer
Dibenzthiazyl disulphide MBTS		1·54	170 °C	Vanderbilt Anchor Monsanto Vulnax Bayer
Zinc salt of 2-mercapto benzothiazole ZMBT		1·64	—	Anchor Monsanto Uniroyal Robinson Vulnax Bayer

(continued)

TABLE 6—*contd.*

Chemical name	*Formula*	*Specific gravity*	*Melting point*	*Suppliers*
Ethylene thiourea ETU NA22		1·45	185 °C	DuPont Robinson Bayer
Tetramethyl thiuram monosulphide TMTM		1·38	104 °C	Anchor Uniroyal Monsanto Robinson DuPont Vulnax Bayer
Tetramethyl thiuram disulphide TMTD		1·42	137 °C	Anchor Robinson Monsanto DuPont Vulnax Bayer
Dipentamethylene thiuram tetrasulphide DPTTS		1·50	112 °C	Robinson DuPont

CHAPTER 2

MIX AND COMPOUND DESIGN

The most widely used and currently available polymers and compounding materials used in the rubber industry and their general characteristics have been itemised in Chapter 1. At first sight, no doubt, the impression gained is perhaps one of confusion, especially to anyone being introduced to the industry for the first time.

Before the War, the initiation was much less painful, as in the main, natural rubber accounted for the largest percentage of rubber used. In order, therefore, to simplify matters, the formulation design of mixes, recipes or compounds will be considered for natural rubber first. Then the differences and common characteristics of the other rubbers at a later stage. There is a lot of common ground as will ultimately be seen. Indeed all the ingredients of rubber mixes can be broken down into general groupings.

In the very early days of the industry the starting point was natural rubber and this behaved in a thermoplastic manner, i.e. the material softened and became tacky when heated; hard and brittle when frozen.

Thus initially we have:

RUBBER

Subsequently, worldwide research and investigation showed that by the addition of sulphur, more 'rubbery' properties were achieved and thus vulcanisation or curing was discovered. (Goodyear USA, 1839; Hancock UK.)

We now therefore have:

RUBBER
SULPHUR

With just these two materials vulcanisation was extremely slow, but with the addition of metallic oxides, such as zinc oxide, an increase in the rate of vulcanisation became apparent. Thus, the process of activation was discovered.

The position now is:

RUBBER
SULPHUR
ACTIVATOR

We now move much nearer to present time, in fact just before World War II, when certain organic compounds (to be called accelerators) were discovered. These materials not only increased the cure rate, but also gave the cured rubber (vulcanisate) vastly improved and superior physical properties.

The situation now becomes:

RUBBER
SULPHUR
ACTIVATOR
ACCELERATOR

Compounds such as these, however, are very difficult to process, and are extremely nervy, i.e. short of mastication.

It is, therefore, necessary to add further ingredients known as fillers to help smooth out the mix. When large quantities of fillers are added (they may be either black or white) it is normal practice to add softeners, which help to disperse the fillers and also counteract, to a degree, the hardening effect of the filler, especially with some carbon blacks.

The recipe now looks like this:

RUBBER
SULPHUR
ACTIVATOR
ACCELERATOR
FILLER
SOFTENER

About this time also, it was found that by the addition of organic antioxidants, the ageing properties of the compound were improved.

Thus, the basic ingredients of most natural rubber compounds are:

(1) Rubber
(2) Sulphur
(3) Activator
(4) Accelerator
(5) Filler
(6) Softener
(7) Antioxidant

There are of course many other ingredients which may be added and which confer special properties to the mix. These will be included in the discussion later, where appropriate.

If the above basic compound is taken, it is possible to sub-divide further and include other currently available materials. However, as will be seen later the above basis applies to the majority of present day polymers:

(1)	Rubber (hydrocarbon)	(a) Natural (b) Synthetic (c) Reclaim
(2)	Vulcanising agent	(a) Sulphur (b) Other materials (depending on polymer)
(3)	Activator	(a) Inorganic (b) Organic
(4)	Accelerator	(a) Slow (b) Medium (c) Fast (ultra)
(5)	Filler	(a) Black (i) Reinforcing (ii) Non-reinforcing (b) Non-black (i) Reinforcing (ii) Non-reinforcing (c) Extenders
(6)	Softeners	(a) Processing aids (b) Plasticisers
(7)	Antioxidant	(a) Staining (b) Non-staining (c) Anti flex cracking

(8) Other materials
    (a) Peptisers
    (b) Retarders
    (c) Stiffeners
    (d) Flame retardants
    (e) Colours and pigments
    (f) Tackifying agents
    (g) Blowing agents for sponge
    (h) Bonding agents
    (i) Reodorants

Armed now with these basic facts, the various ratios of the ingredients within the recipe may be considered. However, before even attempting to formulate a compound, the following points must be very carefully considered:

(1) The finished article must meet the service conditions required and it is, therefore, important to obtain this information accurately, right at the start of the operations.
(2) It is also very important that the compound is designed at the right cost, otherwise the product will not sell. This, however, is a two way condition. It could well be that the service conditions are very severe, so a correct selling price is also required, commensurate with the conditions. It is quite often easy to design if price does not matter. It is also easy to sell, by giving the material and goods away!
(3) Having designed the compound at the correct price level, the material must now be capable of being processed satisfactorily on available factory machines and equipment. This is *essential* for good factory practice to be maintained.
(4) Finally, any specified physical properties must be obtained consistently in the *finished product*, and allowances made for the lower levels of dispersion obtained in the factory (even under supervised conditions), when comparison is made with results from laboratory work. It is a good idea to allow for an approximately 10% fall-off in properties between the laboratory and factory mixed materials.

In order to meet the specified requirements it is of course essential to become familiar with all the basic properties of the various polymers currently available and to blend as appropriate. Quite often it is necessary to arrive at compromises of the above few points and if absolutely necessary to discuss the specification with the customer.

Very often these specifications are not compiled by rubber chemists or technologists, and unfortunately impossible and diametrically opposite properties are written in at one and the same time. If the correct approach is made and once mutual confidences are established, these difficulties can be ironed out with the customer.

It is a widely used practice to base and express all the various ingredient quantities as parts per hundred of rubber hydrocarbon. Thus, as a general guide the ultimately derived basic recipe, discussed previously, would be as follows:

Rubber	100
Sulphur	2·5–3·5
Activator	1–5
Accelerator	0·5–1·5
Filler	As required
Softener	5–10
Antioxidant	1–2

It becomes immediately apparent that an infinite number of permutations become possible between the ratios and amounts of the various ingredients and, indeed, this is the case. The reason for this is that service conditions of most of the individual products are also infinite in possibilities, and a glance at the typical formulations shown later will give a guide and basis from which the exact conditions required can be derived.

At this stage it is considered pertinent also to mention that the vast majority of suppliers of 'rubber chemicals' and synthetic rubbers, etc., to the trade, provide technical back-up to their materials in the form of literature. Subsequently they should be consulted for advice at an early stage if difficulties arise.

MATERIALS

The materials used in these categories all have finite duties to perform within a rubber formulation. Therefore, each will be discussed in the sequence already listed earlier in this chapter.

Rubbers (Hydrocarbon)

Reference should continuously be made to Chapter 1 where the general properties and types of the majority of currently available polymers are listed. In general all of these require mechanical breakdown on conventional equipment (see Chapter 4) and are mixed and compounded using one or more of the techniques outlined in Chapter 3, dependent upon the circumstances.

Reclaim rubber can play an important part in the function of general or specialised compounds especially as a softening agent with natural rubber. Before the War it was used as an extender or cheapening agent, but at the present time it is used in its own right to confer special processing characteristics to specific compounds, e.g. to reduce nerve during processing, to improve adhesion in certain rubber to metal bonds, and also to achieve good tack in friction compounds for use in belts, hose, etc. These properties are conferred because materials such as mineral rubber (MRX) petroleum, coal tar residues and fine oils are used in its manufacture, or within the original rubber formulation from which it was reclaimed. Present day reclaim contains a fairly high percentage of synthetic rubbers.

Vulcanising Agents

As previously mentioned, sulphur was first used by Goodyear in 1839, but not surprisingly other elements from the same group in the periodic table as sulphur, such as selenium and tellurium (and their derivatives) will also function in a similar manner. These are used in specialised applications where good heat resistance is required.

Vulcanisation is the industry term used to describe the process whereby rubbers are reacted with chemicals, usually in the presence of heat, to convert the thermoplastic, uncured state, into the generally accepted 'rubbery' or 'elastic' state. Natural (NR), SBR, polyisoprene (IR), butyl (IIR) and nitrile (NBR) rubbers (just to name a few) all react with sulphur and sulphur bearing chemicals to achieve this. However, with neoprenes (CR) metallic oxides such as zinc oxide and magnesium oxide serve as the vulcanising agents.

Activators

Zinc oxide, stearic (or other fatty acid) are generally found in all recipes based upon NR, SBR, IR, IIR, where they are used as activating materials and produce a uniform rate and state of cure in the compound.

However, they also appear in CR compounds but for different reasons. In this case, the fatty acid helps as an anti-roll sticking additive, whereas the zinc oxide is the vulcanising agent. As well as zinc oxide, the oxides of calcium, magnesium and lead (white, yellow and red respectively) may also be used, to confer special properties, such as increased water resistance in the case of the lead oxides.

Accelerators

As a general guide synthetic rubbers require more accelerator and less sulphur than does natural rubber. This is because in the polymer chain there is a proportion of non-vulcanisable structure which does not require sulphur and in say, SBR, this reduces the reactivity of the butadiene sections of the chain. There is also an important and noticeable difference between SBR and natural rubber with regard to the smaller difference of speed between various classes of accelerator. This is what could be described as ultrafast in NR and becomes medium fast in SBR. These points have to be carefully watched when using blends of NR and SBR.

The accelerators discussed and listed in Chapter 1 should be adequate for the vast majority of operations likely to be encountered in everyday use. However, where exceptions to this are encountered, or if special characteristics are required, then the various accelerator suppliers and manufacturers should be consulted. A general compounder cannot be expected to know everything about each particular process he uses, and should seek the advice of specialists in the field concerned. Much valuable time and perhaps ultimate processing difficulties in the factory can be saved by adopting this policy.

The majority of rubber recipes in use, incorporate organic acceleration, but other rubbers especially CR types and especially the 'G' types, use inorganic oxides, such as zinc oxide, to achieve a state of vulcanisation. Others such as EPDM occasionally use organic peroxides but these are the exception rather than the rule and with full time everyday use, these exceptions will soon be memorised. In the meantime, it is always advisable to check the literature. Indeed even when experienced it is good practice to double check, as errors can and do creep in on occasion.

Fillers and Extenders

As a generalisation fillers can be termed reinforcing and non-reinforcing, and also fall into black and non-black types. The black grades currently available in bulk are listed under raw materials in Chapter 1, and in compounding are of course selected either singly or blended to meet and give the desired properties required of the polymer and product in question.

Dilution with non-black materials, such as china clay, talc and/or whiting is also practised with general rubber, and many industrial goods. This is not only to keep the cost down, which is very important, but also as a device to 'smooth' out the compound to help its processability, especially in extending calendering operations. Practical experience soon indicates just what is necessary to achieve processability, at the right cost levels.

If non-black reinforcement is required, then the pure silica type materials are capable of very good physical properties and are widely used for this purpose, especially with the synthetic rubbers. However, it is still of interest to know that carbon black as an ingredient is still the outstanding reinforcement material for general application, and especially in tyres, to quote Henry Ford 'you can have any colour you like, provided it is black!'

Other materials which very loosely could be called fillers (although extender is perhaps a better or rather the correct word) are factice and mineral rubber. Both of these materials, in their various ways extend the hydrocarbon content, thus helping to kill nerve and assist breakdown of the polymer during mastication and once again making the compound subsequently much 'smoother' to process.

When considering the choice of filler, it is necessary to ensure its suitability in the service environment of the product. As an obvious example, if chemical resistance is required, and in particular resistance to acid conditions, then whiting (calcium carbonate) is unsuitable, whereas inert materials such as silica and silicates (china clay, talcs) are ideal. For extreme acid conditions, then barytes (barium sulphate) is more suitable. This latter material does, however, have a high specific gravity and its volume cost should be closely examined.

Processing Aids

Rubber chemicals within this grouping include peptising agents, softeners (oils and waxes) and plasticisers. A processing aid plays one or more of the roles included in the following list:

(a) ✓ Speeds up the rate of polymer breakdown and also controls the degree of breakdown.
(b) Helps to disperse the other compounding ingredients especially blacks.
(c) Helps to reduce nerve within the compound, and also shrinkage during subsequent processing.
(d) Can impart building tack to the compound.
(e) Improved and more stable compound processing, especially in the compound preparation (blanking) and moulding areas.

Natural rubber is greatly assisted in its breakdown during mastication by the addition of peptising agents. These chemicals act as catalysts for oxidative breakdown during the milling and internal mixer mastication operations. Many of the various proprietary makes of peptiser contain or consist of oil soluble sulphonic acids in selected petroleum bases. Generally speaking peptisers are not required for SBR, CR or EPDM rubbers.

In order to help in the smooth processing of rubbers, especially chloroprenes and at satisfactory temperatures, mineral and/or vegetable oils, petroleum jelly, paraffin, other similar waxes, and chlorinated paraffins (for fire resistance) may be added; the quantity and material type obviously depending on the end properties required.

True plasticisers rather than softeners which are used in the main to impart processability, and assists in adding improved low temperature characteristics to the compound. This principle applies to most polymers, but is obviously dependent on the properties required, suitable materials include phthalates, sebacates, alizarates and organic phosphates, etc.

Antioxidants/Antiozonants

It is almost universally necessary to add antioxidants and/or antiozonants to any polymer to impart improved and satisfactory ageing properties in the cured compound. Some polymers, such as polychloroprenes (CR) and especially butyl and EPDM already have good to excellent 'built-in' ageing characteristics, but even here it is usual and advisable to add small quantities of these rubber chemicals for maximum results. A very important point, not often realised by rubber compounders, is that when a compound is debased, to meet price requirements, it is very necessary to be generous with antioxidant in order to obtain reasonable service life, especially when flexing and bending conditions may be encountered. If some direct sunlight is expected to be encountered, then additionally, small quantities of paraffin wax may be added.

The earlier antioxidants used to help natural rubber life prolongation were based on various aromatic amines and phenols, and even today such materials are still used. It is usual to use quantities of the order of 1 part to 100 parts of polymer, but the amount obviously must and does depend on the service requirements of the product and also upon the actual basic polymer in the formulation. Some antioxidants are specific to the type of protection which they impart, and can be used to improve heat resistance, flex cracking, or improved resistance to weathering, which covers the attack of oxygen and ozone, plus ultraviolet light, temperature variations and moisture.

In addition to organic materials, various blends of microcrystalline/paraffin waxes may be added, and in the correct quantity, dependent upon requirements, will bloom to the surface and form a protective surface film on the product. Provided the film is not broken, even some ozone resistance is imparted to the product.

Ozone attack, however, is more severe than oxygen attack, and whilst most antioxidants impart some ozone resistance to a compound, if ozone is known to be present (i.e. in areas of ultra-violet light concentrations, around areas of electrical discharge, and near to electric motors, especially if they are sparking) then extra antioxidant/antiozonant protection should be given. Additionally, it is a practical fact, despite arguments to the contrary, that in areas of concentrated, exposed seaweed, that extra antioxidant/antiozonant protection is required and advisable.

Miscellaneous Other Materials

Peptisers

This class of rubber chemical can loosely be termed a processing aid, as it speeds up the rate of polymer breakdown and also controls the speed of breakdown. Thus it decreases nerve within the compound, and also shrinkage during subsequent processing. A true peptiser is, in reality, a non-persistent softener, and when used with natural rubber especially, cuts milling and internal mixer times, thus reducing energy. The action takes the form of chemical scission and depolymerisation, but the action is controllable, as it ceases in the presence of zinc oxide.

Retarders

Occasionally, in order to meet specific and difficult requirements, compounds are produced which are extremely 'scorchy' in their processing characteristics, and materials known as retarders may be added, which can be of assistance in this area. Such ingredients are usually acidic in nature, and one well known retarder is based upon salicylic acid/clay dispersion. However, if at all possible it is better to reformulate, as scorchy compounds are indeed a serious menace in a rubber factory, and really should not be tolerated.

Stiffeners

Organic stiffeners are of great assistance where the plasticity of the compound is low, and very small quantities may be added, which in many instances appreciably improve upon this very undesirable state. Such a material is dihydrazine sulphate, and is very effective at concentrations of $\frac{1}{8}$–$\frac{1}{4}$% in many instances.

Flame Retardants

Chemicals which are useful in this category include highly chlorinated materials (both viscous liquids and waxes), and also selenium. With CR rubbers antimony oxide is very useful. Great care must, however, be exercised when using some of these materials because of their poisonous nature, and dispersions of many of them are available, which can be added direct to the mixers without handling.

Colours and Pigments

There are a great number of colours available which are suitable for rubber, and the suppliers' manuals should be consulted for maximum performance for each application. The type of polymer in use must be considered; generally speaking non-staining antioxidants should be used, and the compound base of sufficient whiteness on which to build a good colour. Such white bases may be obtained by the use of lithopone ($ZnS/BaSO_4$) or better still, if costs permit, titanium oxide.

Many colours and pigments available are of course organic, but inorganic materials are still widely used, and include oxides of iron, chromium and strontium, and the sulphides of cadmium and antimony.

Tackifying Agents

The widely used materials in this field include wood resins and coumarone resins. There are also wood distillate residues, such as pine tar and stockholm tar, and their 'so-called' substitutes (which basically are coal tar residues). The latter are very widely used, but in certain processes, their high aromatic contents can cause mould sticking, if care is not taken with the mould lubricants.

Blowing Agents

These materials are an essential component of a sponge recipe, and normally evolve a gas at vulcanising temperatures, which produces the sponge or foam structure. Such materials include sodium bicarbonate (in the presence of excess fatty acid, or oleic type) which liberates carbon dioxide. This produces a continuous or open cell structure, whereas nitrogen produced from organic blowing agents, usually produces unicellular or closed cell structures. Sometimes ammonium carbonate pellets are used, and this produces cells from the liberated ammonia gas. The cell sizes are controlled by the type of blowing agent and speed of blowing.

Bonding Agents

This is a specialised area itself, and the applications are often so specific that they are not of general interest or value. Suffice it to say that if materials such as manganese or cobalt ricinoleates are added to the compound in solvent adhesive form, then bonds to brass and zinc plating can be improved.

Additionally the bonding between rubbers and rayons, polyesters, etc., can be helped by treatment with resorcinol–formaldehyde/latex on the fibre, or by the addition of silica with phenol resins and formaldehyde donors within the rubber formulations.

It is strongly suggested that for any specific purpose, the recommendations of the specialist suppliers of these materials should be sought.

Reodorants

Vulcanised rubbers all have characteristic odours, and after a lifetime in the industry, these tend to be ignored. In the main, they are not unpleasant, but not everybody would agree with this, especially if inhaled in a confined area, at an elevated temperature.

Indeed, each polymer can be identified by practice, and even mixtures of polymers may be detected and identified by an experienced chemist in many instances simply by their distinctive odour.

Deodorants are materials which may be added to some compounds, and which neutralise the characteristic odour of the compound, imparting a clean fresh scent. Even floral and fruity odours may be conferred if desired.

In the case of breathing, wine or food hoses (which are made of high grade rubbers, including pale crepes) the finished product is usually 'sweetened' by the passage of low pressure steam for a short time, thus producing a perfectly acceptable, suitable and safe product.

Typical Formulations

The following recipes are given as a guide only, but may be used as a basis from which the ultimate compound properties required may be derived.

Cables

Insulation recipe

NR	100
Stearic acid	1
MRX	10
Antioxidant	1
Zinc oxide	5
Talc	100
Whiting	50
MBTS	1
Sulphur	3
	271

Sheath

NR	100
Carbon black	45
Rubber process oil	3
Stearic acid	3
Antioxidant	1
Zinc oxide	5
MBT	1
Sulphur	3
	161

Conveyor belts

NR conveyor belt friction recipe

NR	60
Reclaim	80
Peptiser	1
Stearic acid	1
Pine tar	2
Antioxidant	1
Zinc oxide	5
Black	30
MBTS	1
TET	0·1
Sulphur	2
	183·1

NR conveyor belt cover recipe

NR	80
Reclaim	40
Peptiser	1
Stearic acid	2
Pine tar	2
Antioxidant	1
Zinc oxide	5
Reinforcing black	30
MBTS	1
TET	0·1
Sulphur	2·5
	164·6

Ebonite

Hard rubber (ebonite) battery box recipe

NR	25
Reclaim	150
Pitch (MRX)	25
Petroleum jelly	5
Talc	150
Barytes	27
MBT	0·50
Sulphur	45 ✓
	427·50

Flooring

Base flooring recipe

NR	100
Peptiser	1
Zinc oxide	10
Stearic acid	2
China clay	300
MBTS	1·50
TET	0·15
Sulphur	4
	418·65

Colours and pigments may be added as necessary.

Footwear Recipes

Black soles and heels

Reclaim	100
MRX	4
Pine tar	2
Carbon black	50
Zinc oxide	5
Antioxidant	1
MBTS	1·5
Sulphur	1·25
	1·5
	166·25

Brown sole

NR	100
Antioxidant	1
Stearic acid	2
Zinc oxide	10
Coumarone resin	10
China clay	150
Magnesium carbonate	40
Red iron oxide	10
MBTS	1·5
TET	0·15
Sulphur	4
	328·65

Crepe sole

Pale crepe rubber	100
Zinc oxide	1
MBTS	1·5
Sulphur	2·5
	105·0

White sole

Pale crepe rubber	100
Magnesium carbonate	100
Zinc oxide	20
Lithopone	50
China clay	100
Stearic acid	1
Mineral oil	3
Non-stain antioxidant	1
MBTS	1·25
Sulphur	2·50
	378·75

Bathing shoe

NR	100
Stearic acid	1
Zinc oxide	5
Antioxidant	1
Stearin coated whiting	25
MBTS	1
TET	0·1
Sulphur	2
	135·1

Colour pigment as required.

General Purpose Hose Friction Compound

Smoked sheet	30·00
Refined reclaim	30·00
Peptiser	0·25
Calcium carbonate flour	21·50
China clay	10·75
Resin oil	2·25
Pine tar	2·00
Zinc oxide	2·25
Sulphur	1·00
	100·00

Specific gravity—1·23.

General Purpose NBR Hydraulic Hose Lining (Extrusion)

NBR (medium)	37·50
SRF black	40·00
Soft black	8·60
Zinc oxide	2·25
Antioxidant	1·00
Rubber process oil	2·75
DIOS/DAP	3·00
Dark factice	3·00
Stearic acid	0·50
MBTS	0·75
Sulphur	0·65
	100·00

Specific gravity—1·31, T/S (MPa) 10·0 (approx) and E/B (%) 250 (approx).

General Purpose CR Hydraulic Hose Lining (Extrusion)

CR (type W)	30·00
SRF black	21·00
Soft black	10·50
China clay	22·30
Silica	4·00
Octamine	0·50
Microcrystalline wax	1·00
Magnesium oxide	1·25
DPG	0·25
Stearic acid	0·25
Rubber process oil	5·50
Plasticator	1·50
Zinc oxide	1·00
TMT	0·25
Sulphur	0·70
	100·00

Specific gravity—1·59, T/S (MPa) 80 (approx) and E/B (%) 200 (approx).

General Purpose CR Hydraulic Hose Cover (Extrusion)

CR (type W)	37·00
SRF black	42·00
Magnesium oxide	1·50
Octamine	0·75
Stearic acid	0·20
DIOS/DAP	8·25
Light brown factice	7·50
Plasticator	0·25
Zinc oxide	1·50
TMT	0·35
DPG	0·20
Sulphur	0·50
	100·00

Specific gravity—1·40, T/S (MPa) 10·0 (approx) and E/B (%) 220 (approx).

General Purpose Steam Hose Lining and Cover (Extrusion/Calendered)

Smoked sheet	10·00
SBR	24·00
SRF black	20·00
Soft black	30·00
China clay	8·65
Zinc oxide	2·00
Antioxidant	0·75
Stearic acid	0·25
Microcrystalline wax	0·50
Rubber process oil	1·50
MBTS	0·25
TET	2·00
Sulphur	0·10
	100·00

Specific gravity—1·32, T/S (MPa) 7·0 (approx) and E/B (%) 400 (approx).

High Pressure Steam Hose Lining and Cover (Extrusion)

Chlorobutyl rubber	43·00
MBTS	0·50
Zinc oxide	2·00
Calcium carbonate flour	23·45
Stearic acid	0·50
Magnesium oxide	0·20
SRF black	25·50
Petroleum jelly	3·50
TET	0·50
Sulphur	0·85
	100·00

Specific gravity—1·34.

General Purpose Moulded Hose Lining and Cover (Extrusion)

Smoked sheet	5·00
SBR	24·00
Paraffin wax	3·00
Magnesium oxide	1·25
Antioxidant	0·50
MBTS	0·30
Calcium carbonate flour	49·95
SRF black	14·00
Rubber process oil	1·00
Sulphur	1·00
	100·00

Specific gravity—1·56, T/S (MPa) 6·0 (approx) and E/B (%) 300 (approx).

General Purpose Hose Red Cover (Extrusion)

Under lead cure

Smoked sheet	20·00
SBR	20·00
Stearic acid	0·20
Zinc oxide	1·50
Calcium carbonate flour	46·30
Red iron oxide	8·50
Paraffin wax	0·75
Microcrystalline wax	0·75
Antioxidant	0·50
DPG	0·10
MBTS	0·20
TET	0·20
Sulphur	1·00
	100·00

Specific gravity—1·52, T/S (MPa) 6·0 (approx) and E/B (%) 400 (approx).

Proofing

Typical general purpose spreading recipe (heater cured)

Rubber	100
Zinc oxide	16·5
Fine whiting	80
Stearic acid	1
Antioxidant	1
Sulphur	2·5
MBTS	0·5
	201·5

Low rubber content proofing recipe (heater cured)

Rubber	100
Reclaim	150
Dark factice	100
Stearic acid	3
Zinc oxide	7·5
Fine whiting	300
Lithopone	20
Sulphur	2·5
MBTS	0·5
	683·5

Sponge

Brown crepe (well premasticated)	100
Peptising oil	10
Rubber process oil	30
Stearic acid	8
Zinc oxide	5
Antioxidant	1
Stearated whiting	65
Soft black	35
Sodium bicarbonate	15
Sulphur	2·5
MBTS	1
TET	0·2
	272·7

Tyres

NR tyre tread recipe

	(A)	(B)
NR	100	75
Reclaim	—	50
Peptiser	1	1
Stearic acid	3	3
Pine tar	1	1
Zinc oxide	3	3
Carbon black	45	40
Antioxidant	1	1
MBT	3	3
Sulphur	1	1
	158	178

Cycle tread recipe

Reclaim	100
MRX	5
Black	15
Pine tar	2
Stearic acid	1
Zinc oxide	5
MBTS	1
Antioxidant	1
Sulphur	1
	131

NR solid tyre recipe

NR	100
Black	90
Zinc oxide	10
Process oil	3
Stearic acid	2
Accelerator	1
Antioxidant	1
Sulphur	3
	210

Hot water bottles

Hot water bottle recipe

NR	100
Zinc oxide	5
Antioxidant	1
Stearin coated whiting	75
MBTS	1
TET	0·1
Sulphur	2
Colour (pigment)	as necessary
	184·1

Calculation of Specific Gravity

Ingredient	*Specific gravity*	*Quantity*
NBR (Medium)	1·00	37·50
SRF black	1·80	40·00
Soft black	1·80	8·60
Zinc oxide	5·55	2·25
Antioxidant	1·21	1·00
Rubber process oil	0·91	2·75
DIOS/DAP	1·00	3·00
Dark factice	1·05	3·00
Stearic acid	0·85	0·50
MBTS	1·54	0·75
Sulphur	2·05	0·65
		100·00

(1) Divide each ingredient quantity by the specific gravity:

NBR (Medium)	37·50 ÷ 1·00 = 37·50
SRF black	40·00 ÷ 1·80 = 22·22
Soft black	8·60 ÷ 1·80 = 4·78
Zinc oxide	2·25 ÷ 5·55 = 0·41
Antioxidant	1·00 ÷ 1·21 = 0·83
Rubber process oil	2·75 ÷ 0·91 = 3·02
DIOS/DAP	3·00 ÷ 1·00 = 3·00
Dark factice	3·00 ÷ 1·05 = 2·86
Stearic Acid	0·50 ÷ 0·85 = 0·59
MBTS	0·75 ÷ 1·54 = 0·49
Sulphur	0·65 ÷ 2·05 = 0·32
Total	76·02

(2) Sum these figures (= 76·02).

(3) Divide total batch weight by the sum from (2) = specific gravity of compound, i.e. 100 ÷ 76·02 = 1·31. The specific gravity of the compound is 1·31.

CHAPTER 3

MIXING TECHNIQUES

GENERAL

The energy and raw materials problems in the rubber industry originated in the early 1970s, mainly as a result of the oil crisis and seem likely to continue for the foreseeable future. In reality, however, the problem has been present for a much longer period than this, and perhaps really started during World War II due to the fall of Malaya, now part of Malaysia.

Before the War, natural rubber was cheap and plentiful. There was little or no need to conserve materials or indeed, within reason, to worry too much about full utilisation or wastage and scrapping of materials. Furthermore, the only other hydrocarbon available in quantity was CR, which was introduced in the mid 1930s as Duprene, and later to be known as Neoprene (DuPont de Nemours, USA).

When supplies of these rubbers, and especially natural rubber, became restricted during the War, the percentage amount of hydrocarbon in the compounds was progressively reduced, on a phased basis, dictated by governmental decree. This obviously made mixing by conventional methods extremely difficult or indeed impossible, and new techniques were developed to cope with the then unknown problems as they developed. Many of these problems are present today, not only because of shortages, but also because of cost problems brought about by inflation, as a result of the oil problems.

It is therefore considered pertinent to examine the various mixing and compounding techniques not only available at present, but also to review the mixing processes from the 1930s, as many of these techniques, some perhaps now forgotten, will certainly have a place once more in the future of the rubber industry, in the light of energy and material conservation.

It is perhaps true to say that the basic principles of mixing have changed very little over the years, wherever the compounds are mixed. However, due to local conditions and the advent of more and more synthetic polymers, coupled with the obvious need for greater productivity and efficiency, new techniques and methods are continuously being reviewed and introduced. Indeed, the techniques necessary for the satisfactory mixing and compounding of the qualities used are certainly very varied. This is in the main due to the fact that many polymers are used with a wide range of hydrocarbon contents.

RAW MATERIAL STORAGE

It goes without saying that crude stocks should be stored in a convenient position for easy transfer to the weighing out area of the mill room. In addition, the storage temperatures should be uniform (not too low) and the atmosphere obviously dry. Ideally a hot box should be provided for certain grades of polymers, particularly natural rubbers. It is considered pertinent to mention these elementary but important points at this stage, as subsequent operations cannot be guaranteed trouble free, if they are not used.

Powder rooms and weighing areas are generally positioned according to the local geography of both the buildings and the lie of the surrounding land. Extremely efficient operations have been seen where the stores and areas are at ground level, and the weighed batches transferred to the internal mixers via lifts, hoists and conveyor belts. Perhaps the best positioning is for the materials to be stored and weighed on an elevated platform, or in a room level with and behind the mixing equipment.

The amount of mechanisation and automation that can be used for these particular operations depends again on local conditions. In some plants it is possible, because of the large volume of materials used, to have, for example, the rubbers and carbon blacks, all handled and weighed automatically. On the other hand, in a small factory, this is more difficult because of the vast variety of rubbers and drugs used, and also because of the fairly large number of mixed qualities. It is, however, considered that with a little thought and planning, much more standardisation and rationalisation could be achieved than is currently evident in many drug rooms. If for example the carbon black types were examined, and also in conjunction with the white fillers (such as the clays and whitings) then it would, more than likely, become evident that a large degree of rationalisation could be achieved, with many hidden and also direct savings in cost and inventories. This would then allow some bulk handling and automatic weighing to be introduced.

In the various handling systems used within the rubber industry, the basis is generally to break down the mix into several constituent parts. These constituent parts are:

(a) Polymers.
(b) Fillers (blacks and whites).
(c) Small powders including waxes.
(d) Vulcanising materials.
(e) Oils and plasticisers.

The oils may either be fed direct to the mixers or may be pre-blended with the fillers depending on the product and the process. In the case of the carbon blacks, an intermediate bulk handling weight of approximately 1 ton (or 1000 kg) has been introduced between the standard bag and the bulk delivery tanker. This has made possible a semi-mechanised weighing system. In the case of white fillers, where flow properties are not good, vibratory and/or air flotation systems are in use, but these are not as yet 100% satisfactory, and development work is still being carried out.

Mixing Equipment, Cycles and Techniques

As a very sweeping statement, the equipment used for mixing the compounds may be broken down into three categories:

(a) Open mill mixing.
(b) Internal mixing.*
(c) Continuous, automatic and/or high speed mixing.

It goes without saying that the cooling of the mixing equipment at most stages of the process is of paramount importance, and much

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* Banbury—Farrel-Bridge, Castleton, Rochdale, Lancashire. Intermix—Francis Shaw, Manchester. Bolling—Cleveland, USA. Werner & Pfleiderer—Stuttgart, W. Germany.

development time has been devoted by the various makers of the mixing equipment over the years. This without doubt has made the current and faster mixing cycles possible.

For reasons of speed, output and economy, the internal mixing operations are the ones most widely used, but in the GRG field, open mill mixing is still practised, and no doubt will be for many years to come. This is because of the small production runs of certain products, and also where precision dispersion is vital, together with the need for no contamination. Both of these important features cannot be guaranteed with internal mixers.

Open Mill Mixing

Very briefly, the open mill mixing process is to masticate the polymers until an even and smooth band is formed around the front roller. The fillers and oils are added alternately followed by any small additions and finally the vulcanising materials. During the whole operation, cutting and blending by hand rolling is carried out. As the powders drop into the mill tray, they are swept to the front by the operator and added back into the mill nip. The mill tray is usually slightly sloping to help the operator, and a very useful aid is to fit a vibratory mechanism, so that the powder is continuously being returned to the operator, thus saving physical effort.

With those compounds containing mixed polymers, the best dispersion and blending is obtained by individual breakdown of each polymer, and then blending them together while still hot. The addition of the fillers, etc., then follows in the usual way. In order to assist with breakdown, special peptisers may be added during mastication, and in the case of polychloroprenes, retarders and other processing aids may be added very early in the mixing cycle.

Internal Mixing

Dealing next with internal mixers, the 'ideal' set-up is to have two mills in the chain. The first is used to remove the heat from the compound rapidly, prior to the addition of the vulcanising ingredients on the second mill. This also has the advantage of keeping the internal mixer free from curing materials, with far less tendency to scorch problems. It could be claimed that such a system is expensive from the point of view of initial capital cost of plant, but on balance the ease of processing of the resultant compound during subsequent operations more than justifies this. Many factories are indeed installed in this manner. As with open mill mixing cycles, the general rule is to masticate in the mixers, and when the polymer has reached the desired state, the powders, etc., are then added, for mixing and dispersion to take place. The batch is now dropped, passed through the first mill several times and then the curatives are added on the second mill as stated above. It cannot, however, be over-emphasised, that the exact mixing procedure used, whether it be open mill or internal mixer, depends on local conditions peculiar to the particular factory, and indeed upon the wishes and experience of the factory compounder. It is very necessary to be able to keep an open mind on the exact technique to be used, and to select the best combination of circumstances for the occasion. The following techniques, which are widely used, will illustrate the point.

Direct Mixing Process

This means exactly what is stated, in the sense that the compound is mixed, and is then fed directly to the next operation, e.g. either to an extruder or calender. This process obviously requires the accurate planning of the mixer cycle and subsequent operations, and has fairly widespread use. It is very necessary to have tight quality control in operation for several reasons, such as curing and dispersion properties, and also the initial mastication is extremely important because of subsequent 'nerviness', as there is no maturing time in the cycle.

Indirect Mixing Process

In this cycle, the compound is mixed and slabbed off and stored prior to the next operation. The curing materials may be added either before slabbing or just prior to the next operation, after maturing in storage, depending on the particular compound. It is considered that this system (apart from open mill mixing) gives the best compound from a processing angle.

Premastication

In certain instances, particularly in compounds where there is a fairly high hydrocarbon content, it is necessary to premasticate the polymers (to remove nerve), slab off and cool, and then mix in the normal way with this premasticated material. Alternatively, if the compound contains a fairly high filler content, be it either black or mineral, a 'master batch' or 'mother stock' may be first of all mixed, slabbed and cooled, and then final mixed.

Oil Extension

In the case of natural rubber compounds, it is possible to oil-extend, without undue loss of subsequent processing or physical properties, by the selection of a suitable oil and pre-blending this with the requisite carbon black. The 'carboil' so produced is added to the internal mixer with the rubber right at the beginning of the cycle, and the whole is then masticated together. This technique prevents undue chain scission due to mastication, and the resultant plasticity so obtained is very satisfactory. The addition of dihydrazine sulphate* to the compound also helps subsequent processing of such oil-extended natural rubber compounds.

Dump Mixing

Where the compound contains a fairly high proportion of filler, it is sometimes difficult to get the rotors of the mixer to 'bite', and in such cases it is normal to literally dump the whole of the ingredients (rubber and fillers) into the mixer altogether, and then carry on with the cycle. Contrary to old theories, etc., this technique does work, and produces a satisfactory compound for its purpose.

Upside Down Mixing

This technique consists of adding the powders first to the mixer and following this by the polymer. This not only produces a satisfactory mixed material, but also makes it possible to mix certain difficult polychloroprene recipes, which hitherto had to be carried out on open mills because of either scorch and/or sticking problems.

Seeding

This is another extremely useful mixing technique, which was developed during World War II because of shortages of natural

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* Stiffener DSC—Anchor Chemical Company, Manchester.

rubber and other hydrocarbons. It consists of the addition of a small portion of the previous batch of the same material, and allowing the new batch to 'seed' on it during mixing. This is particularly effective in mixing extremely low hydrocarbon content compounds.

Batch Size

It is extremely important periodically to check the wear on both the rotors and shells of the mixers, and to increase the batch weights slightly from time to time to compensate for this, otherwise various mixing difficulties will occur such as dispersion, lack of mastication, etc. It is surprising just how much more good compound can be obtained by these additions, as extra production, before the machine requires reconditioning.

Cycles

There are two schools of thought on the techniques to be used in the mixing cycle of an internal mixer. One is to mix to a fixed time cycle and ignore the ultimate temperature reached; the other is to mix to a fixed temperature rise on mastication, and ignore the total time. Both of these systems produce uniform and economic material from a cost and production angle, but it would be very unwise to say categorically that one was better than the other. In fact, it may even be necessary to operate both systems (in different machines of course) to suit the particular and individual recipe.

Wherever possible it is now current practice to mix as nearly continuously as is practicable. Furthermore, the use of high speed rotors is increasing. This considerably reduces the mixing time but increases the temperatures. Because of this, a lot of work has been carried out on very efficient water cooling systems, and the rapid discharging of the mixed compound. This includes drop doors.

In order further to speed up operations, and by selecting the correct mixing procedure, coupled with accelerator and curing systems, it is possible to direct process mix the whole batch in the mixer. This would not have been possible a comparatively short time ago. Additionally, by mother stocking certain of the more difficult accelerators, it is also possible to add these and blend away rapidly without scorch, right at the end of the internal mixing sequence.

Very recent technology involves use of the so-called Monsanto power integrator which ensures that the mixing is carried out by monitoring and using the electrical energy efficiently, in the correct place, and at the right time, thus ensuring uniform and constant plasticity from batch to batch.

Colour Mixing

'Ideally' (once again it is necessary to use this word) coloured compounds and also light coloured articles should be mixed on open mills or internal mixers in a separate area, and well away from any black batches. Unfortunately 'ideal' conditions are not always possible, and the following procedure is one commonly used, which produces commercially acceptable coloured compounds from an internal mixer used also for black rubbers. In fact, in some plants the mixers are also capable of PVC mixing, being piped up with steam lines to give the necessary temperatures needed for gelling. The 'clean-out' procedure briefly consists of cleaning out the mixer with several batches of premasticated rubber, which are used later for black mixes. The colour mixing now follows, on a sequence of lighter colours first, going darker through the range.

Synthetic Materials

Polychloroprenes have been mentioned earlier, but it is considered worthy of note to mention a fairly new processing material* (specially prepared magnesium oxide, in 'stick' form). This considerably helps dispersion of the magnesium oxide, at the critical stage of mixing, with a reduction in mixing and temperature rise. Thus desirable processing properties are conferred to the mix.

Nitriles are fairly straightforward on open mills, but are rather difficult in the usual type of internal mixer as extremely high electrical energy is required. However, by using specially designed rotor blades, even this material can be made to process well.

Where butyl rubbers are processed, it is desirable to have the mills so positioned as to be able to work safely on the back roll, due to the affinity of this polymer for the faster roll. In large user factories, it is possible to keep butyl rubber confined to its own line, so that it is then practicable to adjust the mill gear ratios so that the rubber is banded around the 'front' roller.

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* Scorchguard 'O'—Newalls Insulation.

Continuous and Semi-Continuous Mixing

In the period before the mid' sixties there had been very little change in the methods or the equipment used within the mixing rooms of the rubber industry. Indeed, the principles and some of the systems used over 100 years ago were still current. It is only perhaps over the past five years or so that systems anywhere near approaching the ultimate goal of continuous mixing have been introduced, and with varying degrees of success. Also in many cases, perhaps at too high a cost when compared with the more established methods. Because of the nature of the various polymers used, the mixing equipment must of necessity be very strong and robust to take care of the very high loads and stresses developed during processing. For example, it is stated that the energy required to compound together all the ingredients of an average passenger tyre tread compound is of the order of 230–290 J/kg (12–15 horsepower min per pound) of stock.[1] This type of quality is very similar to a high abrasion resistant hose and cable cover.

To make either semi-continuous or fully continuous systems of mixing viable, it is very necessary for obvious reasons to have long runs of a limited number of stocks, and therefore very careful planning, rationalisation and standardisation are essential. Short runs on balance are best catered for using the normal and older techniques, as described earlier in this chapter. Perhaps the problems associated with continuous mixing, and for that matter conventional mixing also, may be simplified and identified as two: (a) dispersion; and (b) temperature control of the stock during mixing, with the resultant scorch problems if the latter is not controlled.

If it is assumed that the mixing equipment is at working temperature, and with no further addition of heating or cooling, then all the energy necessary for mixing, except that being used in the various drive mechanisms, will be converted into heat within the stock. If no controls are used on this heat, then obviously the compound could scorch at worst, and at best, would contain latent and very undesirable after processing properties. The equipment is therefore water cooled.

In simplest terms, the resulting heat balance may be expressed as follows:

$$\frac{\mathrm{d}t}{\mathrm{d}\theta} = k\frac{E - H}{\theta}$$

where t = stock temperature
E = total energy consumed expressed in appropriate heat units
H = heat lost to the cooling system
θ = time

Automatic weighing of powders and other ingredients has been in use for some years, and many very efficient systems have been advised, which while they are not fully continuous systems in the true sense, in that the mixing is of a batch nature, they are nevertheless very economical in time, output, cost and quality.

A typical system incorporates an internal mixer (the size of which is chosen to suit the operational conditions in question), and this is fed by the automatic addition of the ingredients, usually minus the curatives. This is because despite the modern and improved systems now in use, there is still more than sufficient heat build-up in the compounds during mixing as to produce scorch conditions in many cases. The mixer may then discharge into a refiner/extruder after which the curatives are added on a mill and slabbed off from a second mill.

Alternatively, the stock may be discharged into a Transfermix* and pelletised still of course without the curatives. By the use of such a machine, it is possible to reduce the times of mixing in the internal mixer and finish off, in the very aptly named Transfermix. At this stage the stock may either be milled and the curatives added, and then finally batched, or if pelletised, the curatives may be added via another Transfermix, cooled, blended and batched off by any of the well known techniques.

The Transfermix consists of a specially shaped screw and barrel, which makes the material pass backwards and forwards through the machine, between the screw and the barrel wall, thus producing shear. The number of passes may be designed into the machine, depending of course on the properties required from the compound. Because of the closeness of the cooling passages within the machine and the compound, excellent temperature control is possible and another good design feature, is that the machine is completely self-emptying, thus ensuring the minimum of batch contamination. Machines have been made up to approximately 500 mm (20 in) screw diameter, with approximate output speeds of up to 15 000 kg/h (33 000 lb).

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* Transfermix—Uniroyal patent.

However, on the debit side, being a single-screw machine, and when used as a mixer, it cannot accommodate large additions of fillers and/or reinforcing materials to give satisfactory dispersion in the available time in the machine. It is therefore, best used to advantage either with an internal mixer set-up, for adding accelerators and other curatives, or indeed as a form of breaking or cracking unit for the feeding of calenders, etc.

Another type of continuous mixer is that designed by Farrell.* This can best be described as a stretched Banbury mixer and its design includes feed screws, mixing rotors and a variable discharge orifice. Once again, the time in the machine to give maximum dispersion is one of the points requiring close attention, and hence the method of feeding is very important indeed. The rotor speeds are variable, which gives a degree of flexibility of masticating and mixing within the limits and confines of available time in the machine. The internal pressure is controlled by the orifice size. Thus it can be seen that, by careful control and permutation of these features, a large degree of flexibility is possible. It is perhaps true to say that this is the best machine of its type for the further development of true continuous mixing with rubber and rubber-like polymers despite a problem with black dispersions.

GENERAL HANDLING OF MIXED COMPOUNDS

After mixing, it is advantageous to blend several batches of rubber together, and it is generally speaking necessary to allow the compound a minimum dwell time of 24 h for maturing purposes. This may sound a little old fashioned, but experience has shown that the best further processing properties of the compound are obtained if this time can be spared. Some processes make it necessary for straining and/or calender grinding (refining) of the compound to take place, prior to its final operations. The systems used obviously depends upon the properties of the compound and its pre-requisites with regard to its next destination.

With the fairly recent advent of the cold feeding of extruders, the question of the best method of feeding these machines arises. Once again this can only be answered locally, owing to the many variables

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* Farrell Continuous Mixer—Farrell, Birmingham, USA.

present. Is the compound, from a plasticity angle, hard or soft? Is it tacky or dry? If too tacky, can it be dusted? And if so, with what? etc., etc.

The problem really resolves itself into strip feeding or pellet feeding. The latter is fraught with many dangers, and a universally satisfactory system has yet to be seen. The former, i.e. strip feeding, is perhaps the best general system, and may be coupled to the direct mixing process previously mentioned by applying rotary knives to the sheeting mill, and taking off through a cooler and finally either festooning on pallets or drumming off. Work worldwide continues in this connection.

LIQUID RUBBER

The future path of continuous mixing could, however, depend very much on the success of the resurrection of the 'so-called' newer technologies of liquid rubber processing and also of powdered rubbers. Over the years, these technologies have had limited success, mainly due to deficiency in materials, methods and processing machinery. However, they currently stand a much greater chance than hitherto, and considerable work is going on in these fields (RAPRA, Shawbury, Shropshire, England).

The rubber industry has always been beset by the physical difficulty of mixing and processing rubber, i.e. the forces necessary during the mixing stage, to break down the material before the fillers and other ingredients may be incorporated and blended in. There is a continual search for an easy and cheaper way of achieving this process. On more than one occasion latex technology has been looked at, as this appears to be a comparatively easy way of getting dispersion and good mixing with the minimum of shear (and hence lower power consumption). There has, of course, always been the same stumbling block—the presence of water and its removal. This led to the use of solvents, with the associated problems of fire and/or health hazards due to the presence of toxic materials. Finally, the rubber was liquefied by melting, thus producing depolymerised rubber, with a viscosity of about 5000 poise at 20 °C. In the 1930s, fillers were added to this material on rubber mills, and excellent insulation material (registered trade name—Kalanoid, BICC Ltd, Leigh, Lancs.) was thus produced. More recently low molecular weight SBR materials have been produced, with viscosities of around 500 poise at 25 °C.

The present difficulty is still to obtain dispersion (and of the carbon black in particular) whilst, at the same time, retaining a pourable material. Another filler is nylon fibre, around 6 mm in length, but in both cases so far the flex resistance is inferior to those of solid rubber. Furthermore, whilst it is possible to disperse in Z blade mixers, the black in particular remains in large aggregates even after prolonged mixing.

POWDERED AND PARTICULATE RUBBER

Powdered rubber mixing is becoming a reality now that nitriles, SBRs, natural rubbers, and other synthetic materials are becoming available in powder, crumb and similar forms.[2] All the compounding materials are blended together in powder blending machinery. They may then either be final mixed in internal mixers, open mills or even directly fed into extruders, with an obvious saving in mixing time and with the added advantage of greater cleanliness. The latter is an extremely important matter, in view of the present effort at controlling pollution.

The more important advantages of powdered rubbers are outlined later and whilst they are specially discussed relative to hose, cables and extrusion, nevertheless, all are applicable to most branches of the rubber industry, and should be viewed and considered as such.

The plastics industry has been using polymers in powder form, particularly those of the thermoplastic type, since the mid 1930s. The first of these to be used in any quantity was PVC, and this was available as a white, free-flowing resin of approximately 1 mm particle size. This incidentally is the separating point, by definition, between powders and granules. It is therefore, surprising that this technology has only very recently become of interest to the rubber industry, despite the fact that the first reference to powdered rubber was in a Dunlop patent dated 1930,[3] and powdered nitrile rubber has been available for some twenty years. It was first produced in this form by Goodrich, in the USA, basically for blending with PVC as a dry and solid plasticiser.

It is therefore, not surprising that much of the basic groundwork on the preparation of powdered polymer should have been done by them. Indeed much of the current bibliography dealing with nitrile materials in powder form has been attributed to and published by them.[4-9]

The author, ever since entering the industry, has considered it strange that the conventional and traditional methods of processing within rubber factories in their mill rooms, over many decades, has been to thoroughly masticate or rather 'knock to pieces' the structure of the polymers, either on mills or in internal mixers, and then hopefully to incorporate fillers, softeners, antioxidants, accelerators, curatives and a host of other items, in an endeavour to undo the damage already done. Then, subsequently, and hopefully, to build the ruptured chains together by crosslinking. The energy used to do this is out of all proportion to the actual needs, and it is not really surprising that many of the strange processing variables and problems that occur without warning in the factory, and then disappear just as quickly, can still remain unsolved mysteries. All those employed within the industry would admit to this and it is considered that energy usage in the very near future will become a very critical factor in mixing rubbers.

Why, then, the time lag? Perhaps it is due to a state of 'egg and chicken' apathy. The rubber industry over the years has been, and still is, very conservative. Because of this, to a certain degree, the suppliers have been in a position to persuade them to take and use what is available. This statement is of course only a very broad generalisation, and fortunately there are many notable exceptions to the rule. Indeed, if it was true, powdered polymers would not currently be available.

In addition to the work on nitriles carried out by Goodrich, Bayer AG (Leverkusen, W. Germany) has also been very active, not only with nitriles but also with poly-chloroprene rubbers, and a complete range of this latter polymer is available in powder form.

Nitrile polymers are now also available in powdered or particulate form from the majority of the main manufacturers, e.g. Chemigum from Goodyear Chemicals Ltd and Breon from BP Chemicals Ltd.

PREPARATION OF POWDERED RUBBER COMPOUNDS

The process widely used for preparing a powdered rubber pre-blend is very similar to that used in the kitchen with a high speed blender, and indeed much of the early laboratory work was done with such equipment. It is recommended that the lid should be fitted securely in position, unlike the experience of the author, some of whose early trials filled the kitchen with carbon black—all, of course, in a very good cause! Powdered rubber compounds lend themselves ideally to automatic powder handling systems, and it is therefore necessary for all the ingredients of the mix to be in powder form before weighing and pre-blending commences; that is, approximately 1–2 mm particle size, with factice and waxes, etc., if used, in fine crumb or flake form. Oils are added direct to the mixer.

For some after-operations, such as completion of the pre-blend by, say, the internal mixer route, particulate technology sized granulated rubber may be used, up to a particle size as high as 12 mm, with perfectly satisfactory results.

Mixing

Just as with PVC and other thermoplastics, the compounding process for powdered rubber mixing consists literally of blending together all the ingredients in the recipe, in an intensive rapid mixer. Suitable machines include those manufactured by Werner & Pfleiderer, T. K. Fielder, Papenmeier, Henschel, and Lodige & Drosna.

These machines have been designed to enable intensive mixing to be carried out and to gain the full effect of the mixing action. The equipment is jacketed so that additional heating or cooling may be used as necessary, depending on the polymer being used.

PROCESSING ON OPEN MILLS

With the nips set tight, it is possible to 'trickle feed' the pre-blend from the storage bin into the mill, and produce satisfactory mixed and uniform material in a remarkably short space of time. Such a system has been observed in several mill rooms, but the operation does tend to be dusty, and efficient dust extraction is essential. Furthermore, because the mill nip is of necessity set tight, the throughput, while greater than conventional open mill mixing is still not as high as when using the compactor route.

Open Mill Mixing—Compactor Route

This system involves the use of a compactor unit* which produces continuous strips of compressed mix from the pre-blend storage

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* Bayer AG, Leverkusen, W. Germany.

container and delivers this material to the mill, with normal nip settings. Very satisfactory and rapid mixing now takes place, so much so that output rates of up to 400% increase, when compared with conventional open mill mixing techniques, are commonplace. Furthermore, dispersion is excellent, with greater reproducibility of results, together with improved physical vulcanisate properties.

Powder Mastication Principle

Effectively, the basic steps involved in the conversion of powdered rubber pre-blends into usable compounded rubbers are as follows:

(a) Compaction or compression.
(b) Deformation to establish rubber–rubber contacts.
(c) Dispersion, especially of the fillers.
(d) Ultimate mixing and homogenisation.

These basic sequences for powdered rubbers apply to open mill mixing or internal mixer sequences, or within other ultimate processes such as direct extrusion or injection moulding.

Internal Mixer Process

If the powder pre-blend is fed directly to an internal mixer, the speed of mixing just as in the case of open milling, is substantially increased once again with cycle time savings of as high as 400%, depending upon the compound, the polymer, and at normal rotor speeds, *not* high speeds. Furthermore, in many instances, two-stage mixing can be completely eliminated, with obvious and immediate reductions in energy usage. This too, is reflected in lower dump temperatures.

As previously discussed, it is not essential to use 1 mm rubber particles in the pre-blend, if the internal mixer route is used. It is possible to obtain satisfactory results with a particle size up to 12 mm in the pre-blend. Indeed, some particulate mixes can even be upside-down mixed, direct in the internal mixer without pre-blending, so versatile is this technology.

Once again the pattern of excellent dispersion, with greater reproducibility of results, is shown as well as, in most cases, improved physical properties.

CONTINUOUS MIXING AND PROCESSING EQUIPMENT

The ultimate aim of powdered rubber technology must be either to continuous mix or process the pre-blend material, and to a large extent this has recently been achieved.[10]

In the USA, the Stewart–Bolling Mixtrumat machine has been developed (Stewart–Bolling Inc., Cleveland, Ohio). This was demonstrated at the ACS Rubber Division 1973 Spring Meeting, where it mixed powder rubber compounds.

Farrel-Bridge, Castleton, Rochdale, UK have introduced their MVX machine, which continuously mixes and extrudes powdered and particulate pre-blend in four stages, namely, feed, mix, vent and extrude. All four stages are automatically synchronised and controlled by the speed of the extruder screw.

Werner & Pfleiderer, Stuttgart, W. Germany, have developed the EVK mixer, basically a continuous machine capable of mixing powder pre-blends, either direct or compacted, as appropriate, or even extruding as the case may be.

Advantages of Powdered and Particulate Rubbers

The main advantages are:

(1) The elimination of the bale cutting operation.
(2) Much shorter mixing cycles than when using either conventional internal mixer or open milling techniques. In the case of some of the high Mooney value nitrile compounds, it is now possible to use the internal mixers, whereas previously only open mills could be used.
(3) Lower power consumption.
(4) Less plant maintenance.
(5) Less capital-intensive plant possible.
(6) Better ultimate dispersion.
(7) Possibility of more rapidly accelerated compounds being mixed.
(8) Considerably less heat memory retained when using some of the more difficult polymers such as polychloroprene, and hence less scorch tendency.
(9) Possibility of direct feed to the extruders and moulding presses, thus eliminating the internal mixer and/or open milling operations.

(10) No need for premastication and masterbatching.
(11) Easier control in the factory.
(12) Considerably lower dump temperatures after mixing.
(13) Better environmental conditions.

These advantages are dealt with in more detail below.

Bale Cutting Eliminated

Bale cutting of the various polymers is part of the everday processing in all rubber factories, and is both fairly highly capital-intensive and labour and time consuming. For obvious reasons, if the powder route is being used, as the polymer is already in a directly and easily usable form, the bale cutting operation can be eliminated.

Shorter Mixing Cycles

A normal GRG type of internally mixed compound, by direct process, takes approximately 10 min to mix, in say a No. 3 Banbury mixer, depending upon the formulation and the polymer. Some mixes can take up to 12 min and even longer if two-stage or master batch processes have to be used. As a general statement, using powdered polymers, not only can master batching be eliminated but the mixing cycle can be drastically reduced. Satisfactory mixes using pre-blends can be dropped from the mixer in a mixing time of 2 min and in a time as low as 3 min by the use of non-pre-blended material, and with satisfactory physical and processing properties (Table 7).

From Table 7 it can be seen that internal mixer outputs can be increased at least three-fold by the direct mixing of powdered polymer, weight for weight, with baled polymer, or outputs of at least four-fold with pre-blends of the whole mix via the intensive mixer initially. The physical properties are also at least equal to, or an improvement on, the controls. The improvement of physical properties occurs in both T/S and E/B, at the same time. This is a common occurrence with powdered rubber compounds.

Power Consumption

Without doubt there is less power used in the internal mixer, when powders rather than bales are used. For example, the fact that more batches per unit time can be mixed, as is shown in the 'shorter mixing

TABLE 7
MIXING CYCLE COMPARISONS

Polymer	*Internal mixer*							
	2-stage mix (control)		*pre-blend 2 min*		*non-pre-blend 3 min*		*straight mix 10 min*	
	T/S[a]	*E/B*	*T/S*	*E/B*	*T/S*	*E/B*	*T/S*	*E/B*
NBR	109	160	118	180	116	175	—	—
CR	—	—	113	240	114	240	112	235
NR/SBR	—	—	95	590	98	585	87	560

[a] T/S = kg/cm^2.

cycles' section above, is one proof. Furthermore, the lower dump temperatures prove that less energy has been used, and this is also confirmed by the internal mixer electrical load charts (Table 8).

Perhaps one of the most graphic demonstrations of the value of powdered rubber technology was seen during the energy crisis in the early 1970s, when a three-day week had to be operated, with only 65 % of normal power requirements. By the use of powdered rubber, rather than baled rubber, 95 % of the normal five-day bale output was achieved, without exceeding the 65 % energy restriction, and in three days of operation.

Less Plant Maintenance

As has been mentioned, it is a fact that more batches may be mixed per unit time; as a simple example, it is possible to eliminate at least one

TABLE 8
POWER CONSUMPTION COMPARISONS

Polymer	*Control*		*Powder mix (same recipe)*	
	average dump temp. (°C)	*max. amps*	*average dump temp. (°C)*	*max. amps*
NBR	140	220	115	145
CR	145	170	115	135
NR/SBR	150	165	110	125

shift from the three normally operated, and still achieve the same volume output. Thus, there is an immediate maintenance saving of 33%, plus many other fringe benefits. The whole mill room operations should be closely examined to see where savings of time, etc., can be achieved, with the obvious ultimate savings in plant maintenance.

Less Capital–Intensive Plant Possible

This is a very obvious fact, that as more output is achieved in unit time, less heavy mixing plant is required than hitherto, on a weight for weight basis, with obvious processing cost improvements. Furthermore, if the direct pre-blend powder route is in operation, then there will be an obvious reduction in the very heavy processing equipment normally used in the mill room.

Better Ultimate Dispersion

Rheograph traces confirm this, and physical tests taken from factory mixed material correlate much more closely with those obtained from laboratory mixed batches. It is customary, with bale mixed material, to apply a factor of approximately 10% to allow for fall-off in properties due to the dispersion being lower from the factory compound. This is not necessary with powder based compounds.

Greater Acceleration of the Curing System Possible

This is an established fact, with heavy loaded compounds, plus high acceleration which normally must be mixed on open mills because of the high temperatures reached, can now be mixed in the internal mixer. This particularly applies to NBR loaded compounds, and also to some CR qualities.

Less Heat Memory—CR Rubbers

Polychloroprene is a polymer which has a heat memory. This means that at all stages of processing, the heat so developed is additive and accumulative within the polymer. Thus, unfortunately, particularly in high-loaded type compounds, the basic and already difficult scorch properties are aggravated. Since powdered rubber compounds mix and process cooler (as has been discussed), the accumulative build-up of heat in the compound is considerably reduced, and hence scorch tendencies are almost eliminated and subsequent processing properties improved.

Direct Feed to Extruders/Moulding Presses

Work has shown that this is now an established processing fact.[2,10]

Possibility of Elimination of Premastication and Masterbatching

Indications are that certainly several masterbatching operations can be eliminated, depending upon the polymer and the end product. Additionally, the results of the work shown under 'shorter mixing cycles' are very applicable. Obviously, each set of local conditions will require examination, but the result of the exercise will be very worthwhile.

Easier Control in the Factory

Because of the comparative simplicity of the powder route process, easier factory control is an immediate and obvious fringe benefit. Indeed, the development of the dispersion measurement test from the ASTM T/50 method, as a process control test, has already proved itself in bulk factory manufacture.[2]

Lower Dump Temperature from Internal Mixer Route

This very advantageous property of the powder route, via internal mixers, is linked closely with the fact that lower power consumption is needed due to the physical form of the polymer presented to the mixing machines. Table 9 using exactly the same compound but either

TABLE 9
TEMPERATURE COMPARISONS

Polymer	*Dump temperature (°C)*	
	control (bale)	*powder*
NBR	140	115
CR	145	115
NR/SBR	150	110

in bale or powder form, confirms this point. Because of lower dump temperature, there are also less fumes on discharge.

Better Environmental Conditions

The mixing and mill room areas of many rubber factories are dusty, and this is obviously not desirable. Indeed, in the UK, as a result of the Health and Safety at Work Act 1976, maximum atmospheric threshold limit values are laid down for the various materials used in rubber formulations.

The use of powdered rubber pre-blends enables all the materials to be bulk handled in a closed system, thus making possible extremely clean and dust-free working conditions. Furthermore, because powdered rubber processes much cooler than the bale counterpart of the same recipe, there are less fumes during the various processing operations.

Energy and Economic Considerations

Traditionally, the rubber industry has used very heavy and robust mixing equipment in the mill-room area. This has been necessary because of the need, right from the early origins of the industry, to masticate the natural rubber, to the right viscosity, prior to the addition of the other compounding ingredients. Obviously, there has, therefore, been a very high energy usage. Regretfully, this energy has always been there, irrespective of cost, although until the early 1970s it has usually been relatively cheap. The cost of the energy used within a mixed compound, in general, has been a very small percentage of the total mixed cost. However, the time (although long overdue) is now opportune for examination, not only because of the actual present high price of electricity, but also because of predicted future shortages and the real need for energy conservation.

Without doubt, one of the very fertile areas to examine, with regard to energy savings, lies in the field of powdered and particulate rubbers.[2] The use of polymers in this form has been rather slow to gain acceptance, but is now gaining momentum worldwide, and especially in Europe. It has already been shown that because of the smaller particle size of particulate rubbers, more batches of compound can be mixed per hour, and using less energy.[2]

It is occasionally argued that the energy savings achieved are less than claimed because of the grinding operation used in some cases, for obtaining the particulate material, and this obviously has to be taken into account.

However, there are manufacturing routes available, which do not involve the drying, baling, and subsequent grinding of the coagulum at the later stage, but rather use to advantage the small particle size already present. This currently does not apply to all polymers, but it is confidently anticipated that in the future this route will be widely followed.

So-called friable bales are already available, which are an intermediate state between full bale and particulates, and these are also energy savers in the mixing processes (SBR and NBR).

Closely allied with cleanliness, and energy savings, and the coagulum route, is the so-called polyblack process (Polyblack, BP Chemicals, Barry, South Wales). This involves the introduction of carbon black in wet form to NBR latex, thus producing a very clean black masterbatch in friable, and clean crumb form. This is then capable of processing either through the internal mixer route or other direct particulate route.

Thus, it can be seen that grinding is not always necessary, but if grinding has to be used, then a much smaller sized particle starting point than a bale, is possible, with a very obvious reduction in grinding energy.

It is the final grinding operation, i.e. from particulate to true powder (1 mm), that adds time, cost, and energy to the 'powdering'. Consequently, unless a direct process route using true powder form is to be operated, particulates of up to 10 mm size should be considered in conventional internal mixing equipment.

Furthermore, one major advantage, of a new machine (MVX Machine—Farrel-Bridge, Castleton, Rochdale, Lancs.) is that it is capable of direct processing pre-blend particulate polymer in many instances,[10,11] with considerably better processing characteristics of the mixed stock and and also improved physical properties when vulcanised (Table 10).

Returning to the use of polyblack NBR, apart from cleanliness, it is possible in the case of hose compound, and those used elsewhere, to completely eliminate the two-stage mixing operation. This has previously been essential, because of the necessary basic hardness of the stocks with regard to viscosity. Thus, here there is considerable energy saving potential, and once again with improved physical properties (Table 11).

TABLE 10
MVX COMPARISON

Polymer	*Control*		*MVX processed*	
	T/S (*kg/cm*^{2})	*E/B* (%)	*T/S* (*kg/cm*^{2})	*E/B* (%)
NBR	109	160	129	204
CR	112	235	117	244
NR/SBR	87	560	99	590

Work within the mill room areas has shown considerable energy savings by the use of powdered and particulate rubber (up to approximately 10 mm). Typical energy usages and savings are shown in Tables 12 and 13 for each operation in bale and particulate form, and in typical extrusion routes respectively. It must of course be realised that many of these results have been obtained from very high Mooney, hydraulic and other hose compounds. Hence, some of the energy values quoted could well be higher than other branches of the rubber industry. However, irrespective of the type of compound used, the comparisons are very valid, and show savings with the use of particulates.

Tables of each processing operation should be compiled for both bale and particulate, over say at least one typical week's production, and the total kWh of electricity used, plotted against the total weight (kg) of compound processed. It is then a simple matter to obtain a very accurate kWh/kg reading for each operation; and under the conditions prevailing in each particular factory and operation.

TABLE 11
NBR/POLYBLACK COMPARISON

Test	*Control (bale) 2-stage mix*	*Polyblack crumb*
T/S (kg/cm^2)	109	132
E/B (%)	160	250
Compression set (%) 24 h at 70 °C	25·8	20·8
Relative density	1·35	1·35
T/50 value	−15 °C	−15 °C
Cabot rating	4·5	5·0

TABLE 12

ENERGY USAGE—BALE RUBBER

Operation	*kWh/kg*
Bale cutting	0·32
Banbury—Stage 1	0·97
Banbury—Stage 2	0·97
Open mill	9·02
Cracker mill	0·52
Warm up mill	0·52
Hot feed extruder	0·39
Cold feed extruder	0·64
Calendering	0·77
Powder/Particulate (1 mm/6 mm)	
Intensive mixing	0·06
Compacting	0·13
Milling	0·06
Blend (Banbury)	0·52
Blend (mill)	2·26
MVX	0·64
Direct extrude	0·90
Direct injection moulding	0·32

TABLE 13

ENERGY USAGE—EXTRUSION ROUTES

Bale route	*kWh/kg*
Bale cutting	0·32
Banbury—Stage 1	0·97
Banbury—Stage 2	0·97
Mill 1	0·52
Mill 2—Strip	0·52
Cold feed extruder	0·64
Total	3·94

Powder/Particulate route	*Banbury*	*MVX Strip*	*MVX Direct*
Intensive mixing	0·06	0·06	0·06
Banbury	0·52	—	—
Mill 1	0·52	—	—
Mill 2	0·52	—	—
MVX	—	0·64	0·64
Cold feed extruder	0·64	0·64	—
Total	2·26	1·34	0·70

Economics

If economics are ignored, there is no doubt that particulate rubbers could be used at once, and in all branches of the rubber industry, as a major source of energy saving. If energy becomes so precious that it *must be conserved*, then once again particulate rubbers would be part of the answer to compound mixing.

In the meantime, however, the premium cost of powdered/particulate rubber cannot be ignored. Therefore, it is essential that all aspects of the operating process should be closely examined; and subsequently existing stages can be eliminated or speeded up. To establish this, flow charts should be drawn of the current methods in use, and then compared with the system which could be used with the powder route.[2,12]

A useful formula for this calculation is:

$$\text{Conversion cost/kg} = \frac{M + F + V}{R}$$

where M = the manpower (wage rate × number of men)
F = the fixed costs (overheads = depreciation = maintenance)
V = the variable cost (energy, etc.)
R = the mixing rate (kg/h)

If this exercise is carried out for each particular process, and the savings (if any) set against the power/particulate premium of the polymer, it is then quickly apparent which route should be taken. In the majority of cases, the scales will be tipped in favour of particulates.

DISPERSION

In any rubber compound it is essential that good dispersion of all the compounding ingredients is achieved, in order to optimise the properties of the particular recipe.

The methods normally used for deciding the correct degree of dispersion in a compounded recipe include measuring tensile strength and elongation at break at various stages of cure, and then plotting the tensile product (TS and E/B) and examining the 'plateau' in the curve. Additionally, modulus and perhaps tear strength, hardness, and compression set may also be used as criteria. These tests give a reasonably accurate measure, but unfortunately take rather a long period of time. Therefore, they are not ideally suited as routine factory quality and process control checks in the high speed context of power blending and mixing techniques.

Other methods are those developed by Cabot Carbon Ltd (Cabot Torn Rating Chart) and Dunlop (H. Leigh-Dugmore, Dunlop Ltd, Central Research Division, Birmingham, UK) using visual and transmitted light standards to compare the torn surfaces. Indeed, these are quite accurate, although once again require time and a fair degree of skill of assessment during the fixing of the rating. Electrical and other microscopic techniques have also been developed, but for obvious reasons very few routine control laboratories have all these facilities.

It is therefore evident that a rapid and accurate system is required to ensure adequate mixing and its measurement on a production basis. Such a method developed from the old T/50 test, which was a means of measuring the state of cure, by low temperature techniques, is worthy of consideration.

The T/50 value is the temperature at which 50% recovery of the specimen has taken place after a cured dumb-bell sample has been stretched by 100%, frozen in a bath of acetone–alcohol–carbon dioxide mixture, and allowed to regain temperature.

This is a very rapid and accurate means of determining the state of cure, and while generally used for natural rubber compositions it is also applicable to many other polymers, including SBR, NBR and CR, because of the relation between the T/50 value and the glass transition point of the polymer. This value is quite clear, distinct and reproducible for each compound.

It is assumed that in using this technique, and contrary to some theories, this has been shown to be so in practice (when comparing with the other dispersion methods); if the smallest ingredients in the compound weightwise, namely the curatives, activators and accelerators, are correctly and evenly dispersed, then the state of cure at the appropriate time and temperature must be, and indeed is, correct.

If, therefore, the small items are well dispersed, it is a reasonable assumption that the large quantity fillers, including the blacks and inorganic materials, are also well dispersed. For any particular compound, there is a finite T/50 value, and this correlates well with the Cabot rating. Thus, the T/50 test can be used as a very rapid and

TABLE 14

T/50—CABOT COMPARISON

Results Sample no.	*Nitrile*		*Polychloroprene*		*Natural rubber/SBR*	
	T/50 value (°C)	*Cabot rating*	*T/50 value (°C)*	*Cabot rating*	*T/50 value (°C)*	*Cabot rating*
1	−15·0	4·5	−22·5	4·3	−33·0	4·8
2	−15·0	4·5	−22·5	4·5	−33·0	4·5
3	−15·0	4·5	−22·5	4·5	−33·0	4·5
4	−15·0	4·5	−22·4	4·5	−33·0	4·3
5	−15·0	4·5	−22·5	4·5	−32·9	4·5
6	−14·9	4·5	−22·5	4·8	−32·9	4·5
7	−15·0	4·5	−22·5	4·5	−33·0	4·5
8	−14·9	4·5	−22·5	4·3	−33·0	4·5
9	−14·9	4·5	−22·5	4·5	−33·0	4·5
10	−15·0	4·3	−22·4	4·3	−32·9	4·3
11	−15·1	4·3	−22·4	4·8	−33·1	4·5
12	−15·1	4·8	−22·6	4·8	−33·1	4·5
13	−15·1	4·5	−22·5	4·5	−33·1	4·5
14	−15·1	4·5	−22·6	4·3	−33·1	4·5
15	−14·9	4·5	−22·6	4·3	−33·0	4·5
16	−15·0	4·5	−22·5	4·8	−33·1	4·8
17	−14·9	4·5	−22·5	4·5	−32·9	4·5
18	−14·9	4·5	−22·4	4·5	−32·9	4·5
19	−15·1	4·5	−22·5	4·5	−33·0	4·5
20	−15·0	4·5	−22·6	4·5	−33·0	4·5
Average	−14·995	4·5	−22·5	4·5	−33·0	4·5
Standard deviation	0·0745	—	0·063	—	0·07	—

handy practical control for dispersion. Table 14 shows the reproducibility possible under controlled conditions. The T/50 method is ideal for powdered and particulate rubber compounds.

ADHESIVES AND DOUGHS

The usual method for producing adhesive and dough materials is to masticate the compounds concerned to a very low plasticity so as to render them very soft. After slabbing and storage, the compound is then warmed-up and given further mastication on a two-roll mill, and then sheeted out very thinly to approximately 1 mm thick. The thin sheet is then earthed (to remove static electricity), and is placed in a rectangular metal box, complete with lid, and covered with the appropriate solvent for that polymer. Layers of polymer and solvent are then alternated, until the bin is filled and then the lid is placed in position. This operation in the process is known as 'laying-down'. The solvent now swells the compound and after about 96 h the swollen mass is cut with a spade and transferred to a Z blade, ball mill paddle or similar mixer for final mixing. At this stage more solvent is usually added to bring the final viscosity and/or the total dissolved solids to the desired levels of consistency.

This particular branch of the industry is an obvious *must*, for powdered rubber technology, as it is possible with a powdered rubber pre-blend to completely eliminate the laying-down procedure, thus enabling the pre-blend to be placed at once in the mixer with the solvent, and complete a satisfactory adhesive, solution, or dough within hours, rather than days. Also, if incorporating into the system carbon black/NBR mixtures (Polyblack—BP Chemicals Ltd), exceptionally smooth, rapid and uniform doughs can be produced.

Typical commercial solvents used in this industry are:

NBR	Toluol or chlorinated solvents
CR	Toluol or chlorinated solvents
NR	Petroleum naphtha
SBR	Petroleum naphtha
EPDM	Petroleum naphtha

It is essential, when handling solvents, that great care is taken with regard to fire hazards, static electricity and TLV limits, etc.

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CHAPTER 4

GENERAL PROCESSING PLANT AND EQUIPMENT

Raw materials, the building up of rubber compounds from them and the various methods of mixing available to the industry have been discussed in the previous chapters. The actual heavy machinery most used to achieve this will now be discussed. Before using any of them, however, it is essential to ensure that adequate guarding, in accordance with the factory acts, is in position, and operational. Rubber machinery can be extremely dangerous if mishandled, but is perfectly safe if the rule book is adhered to and not treated with contempt. It is also very important and lawful that adequate training is given to the operatives, so that safe handling will automatically follow.

Open Mills

These consist of two parallel rollers, adjustable for nip distance setting. Sizes range from approximately 12 in long for use in laboratories to as long as 84 in. Common sizes are 60 in and 84 in mills, and installation can be either single, in pairs, or indeed of several in line, depending on operating conditions required in the particular factory concerned. Roller speeds vary from even speed to ratios as high as 1:1·2 for grinding purposes. Common speeds for general purpose work are approximately 1:1·05. Figures 1, 2 and 3 show laboratory mills and typical mills of the single and double variety. The safety bars can be clearly seen.

Internal Mixers

The two types most widely used, worldwide, are the Banbury mixer and the Intermix machines. Figures 4 to 9 show various sizes of

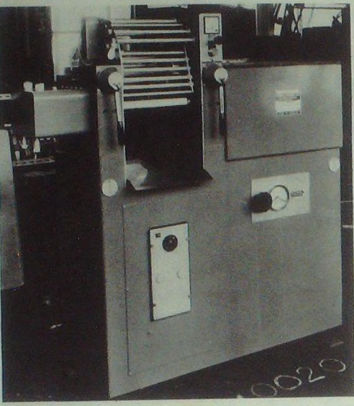

FIG. 1

Laboratory mill. (*Courtesy*: Farrel-Bridge, Rochdale.)

FIG. 2

Single mill. (*Courtesy*: Farrel-Bridge, Rochdale.)

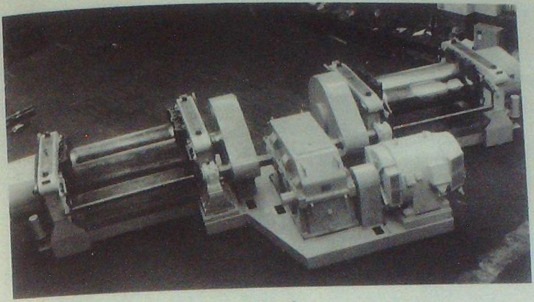

FIG. 3

Double mill. (*Courtesy*: Francis Shaw, Manchester.)

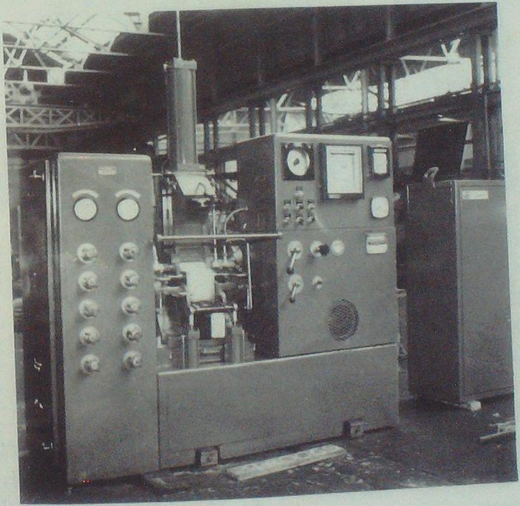

FIG. 4

Laboratory Banbury. (*Courtesy*: Farrel-Bridge, Rochdale.)

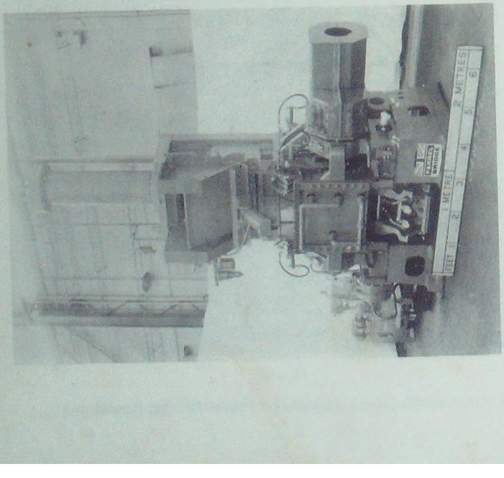

FIG. 5

Banbury mixer. (*Courtesy*: Farrel-Bridge, Rochdale.)

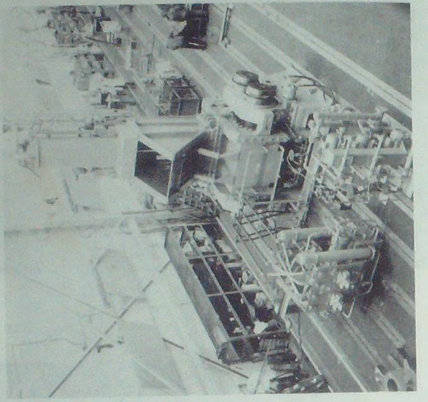

FIG. 6

Banbury mixer. (*Courtesy*: Farrel-Bridge, Rochdale.)

Banburys and Intermixes respectively, ranging from the laboratory size to large scale factory machines.

Banbury and Intermix machines work on two entirely different principles, whilst achieving the same objective, i.e. adequate mixing and dispersion of the ingredients at satisfactory mixing speeds.

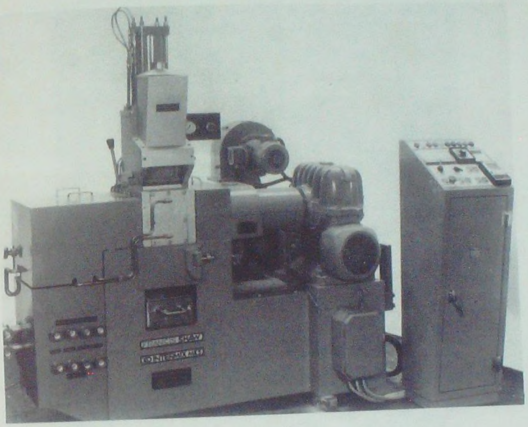

FIG. 7

K0 Laboratory intermix. (*Courtesy*: Francis Shaw, Manchester.)

Perhaps the best way to describe the two machine mixing principles is to quote from the latest literature kindly provided by the two makers, and which is highly recommended for further reading, as mixer capacities and sizes are also listed.

Banbury—(Farrel-Bridge 'F' Series)

The Banbury mixer consists of three major assemblies, the feed module, the mixing module, and drive module.

The feed module incorporates the feed hopper section through which materials to be mixed are introduced, and also the weight

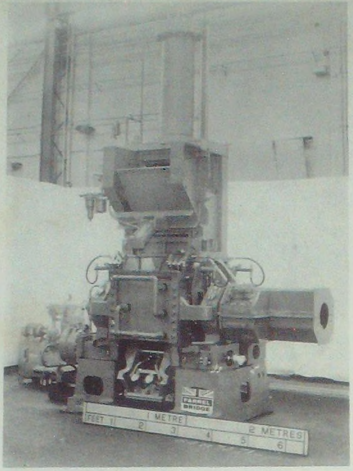

FIG. 5

Banbury mixer. (*Courtesy*: Farrel-Bridge, Rochdale.)

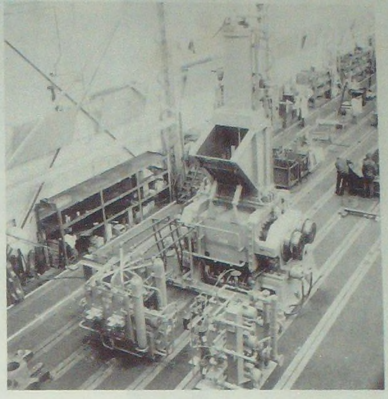

FIG. 6

Banbury mixer. (*Courtesy*: Farrel-Bridge, Rochdale.)

Banburys and Intermixes respectively, ranging from the laboratory size to large scale factory machines.

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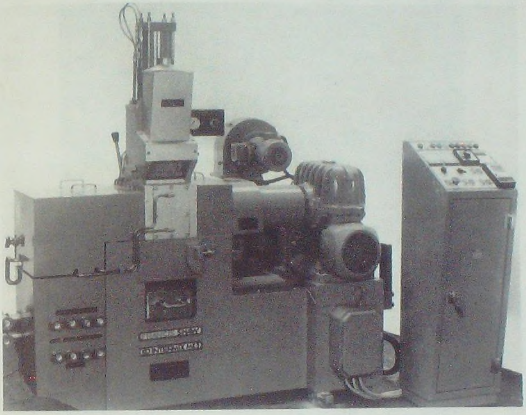

FIG. 7

K0 Laboratory intermix. (*Courtesy*: Francis Shaw, Manchester.)

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Banbury—(Farrel-Bridge 'F' Series)

The Banbury mixer consists of three major assemblies, the feed module, the mixing module, and drive module.

The feed module incorporates the feed hopper section through which materials to be mixed are introduced, and also the weight cylinder and floating weight to force these materials into the mixing chamber.

The mixing module includes the enclosed mixing chamber, rotors and the drop-door assembly for discharging the batch. The rotors turn in opposite directions and at differing speeds to keep the material in constant circulation. Mixing is accomplished by four different actions: milling, kneading, longitudinal cut-back and lateral overlays. Milling is the high shear action of the rotors smearing material around the periphery of the chamber bores.

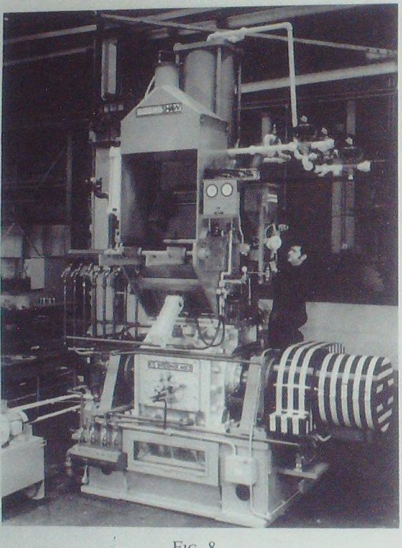


FIG. 8

K5 intermix. (*Courtesy*: Francis Shaw, Manchester.)

Due to the helix angles of the rotor blades, material is moved towards the centre of the mixing chamber, thereby causing longitudinal cut-back. Because of the different rotor speeds an

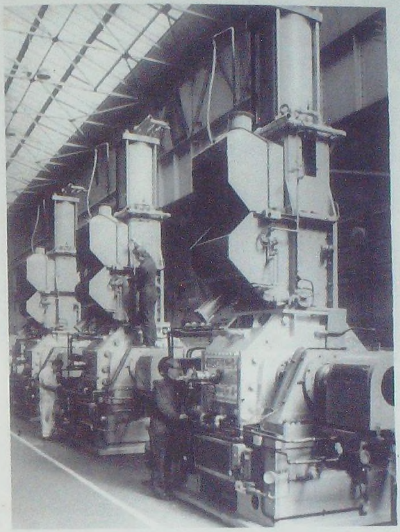


FIG. 9

K6 intermix. (*Courtesy*: Francis Shaw, Manchester.)

intensive kneading action takes place between the rotors and lateral overlays from one side of the chamber to the other.

These four actions, together with correct temperature control of the mixing chamber, result in high quality compounds with relatively short mixing cycle times. Banburys have been in use for approximately 60 years, and some 2500 have been made and are in worldwide use.

Intermix (Francis Shaw Mk3)

In the Intermix the two rotors are large and have interlocking projections (nogs) and they run at equal speeds. Each rotor has one large helical projection and two small projections. Distribution of stock around the chamber is achieved by the screw action of the helical projection, and these are arranged so that each rotor propels the stock longitudinally in opposite directions. Dispersion of powders into the loose material is achieved in the nips between the nog periphery and the adjacent rotor body diameter, where a friction ratio is present due to the difference in peripheral speeds of the helical nog outside diameter and the rotor body diameter. The screw action caused by the helical nog, combined with the small friction ratio in the nip between the rotors, gives an action which simulates that of a two roll mill; that is dispersion caused by the friction ratio in the nips and distribution caused by cutting and rolling across the mill face. The two roll mill has always been recognised as an excellent mixing machine, and this arises from the large area of cooled metal surface in contact with the batch, combined with a low friction ratio and narrow nip. These characteristics are retained in the Intermix rotor design. Additionally, good heat transfer was kept in view when the other mixing chamber components were designed.

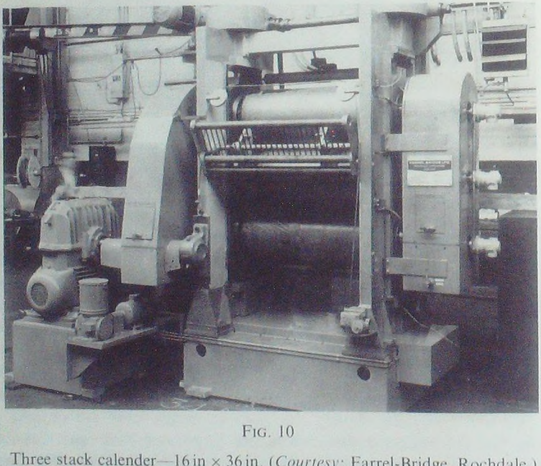


FIG. 10

Three stack calender—16 in × 36 in. (*Courtesy*: Farrel-Bridge, Rochdale.)

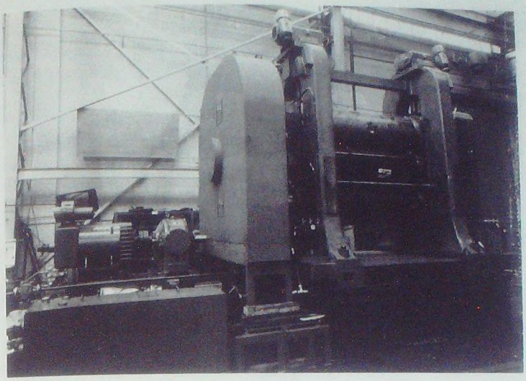


FIG. 11

Three stack calender—24 in × 68 in. (*Courtesy*: Farrel-Bridge, Rochdale.)

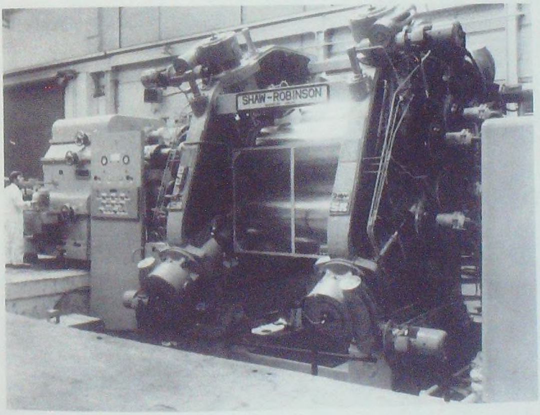


FIG. 12

Four roll Z calender—26 in × 72 in. (*Courtesy*: Francis Shaw, Manchester.)

Calenders

Calenders are used for producing rubber in sheet form or when used with friction ratios to friction fabrics. They are also used for doubling sheets together or 'topping' sheet rubber on to friction or spread coated fabrics. Figures 10 to 12 show typical calender bowl configurations and also give an idea of size.

MOULDING

Moulding Presses

Conveyor Belts
Figure 13 shows a typical press for vulcanising conveyor belts, while Fig. 14 is used for the continuous vulcanisation of the lighter weight type of flat belting.

Tyres
Figures 15 and 16 illustrate modern 'Bag-o-Matic' tyre curing presses.

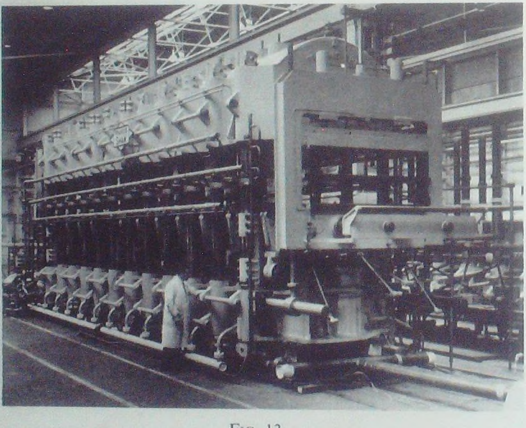


FIG. 13

Conveyor belting press. (*Courtesy*: Francis Shaw, Manchester.)

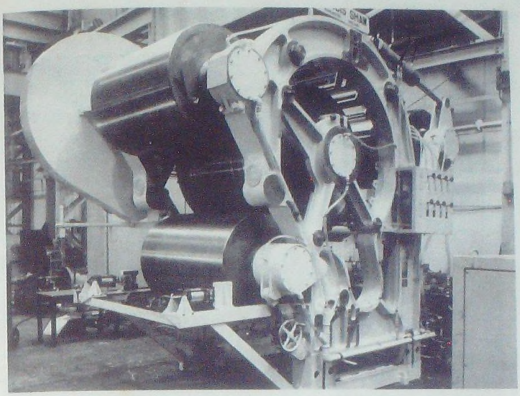


FIG. 14

Rotocure. (*Courtesy*: Francis Shaw, Manchester.)

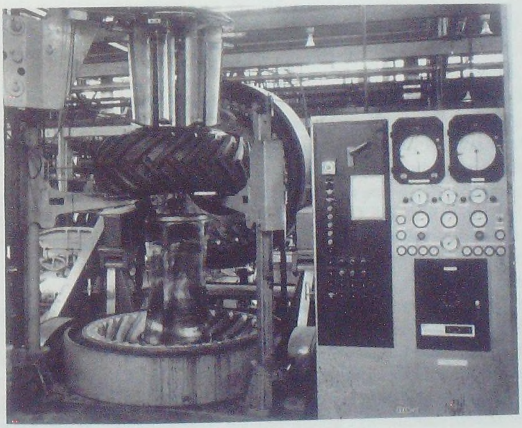


FIG. 15

85 in Bag-o-Matic tyre curing press. (*Courtesy*: Francis Shaw, Manchester.)

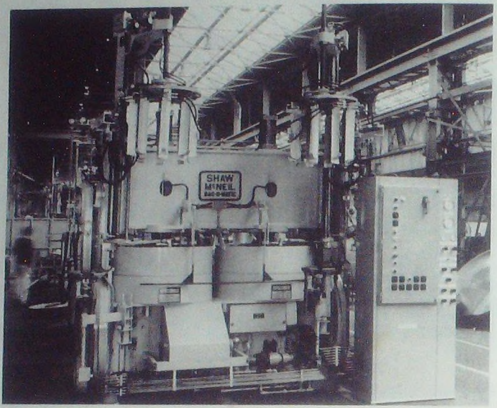


FIG. 16

42 in Bag-o-Matic tyre curing press. (*Courtesy*: Francis Shaw, Manchester.)

Mechanicals

Conventional compression moulding techniques require the preparation of blanks in the pre-moulding operations, and these are made from conventionally mixed compounds, and then 'clicked' out from sheets or slabs, or from screw and/or ram extruded sections.

Figure 17 shows a typical GRG press for mechanical mouldings. This branch of the GRG side of the rubber industry presents an interesting challenge for powdered rubber technology. If powdered technology principles are applied to these operations, it is immediately apparent that here is a possible area for its use.

Early attempts to compression-mould compounds direct from powder pre-blend were unsuccessful, until compacting by pelletisation had taken place. The problems were caused by entrapped air and spillage of the powder due to movement when closing the press. However, when pills (pellets) were fed to the compression mould, satisfactory mouldings were produced from some materials, having low Mooney plasticity characteristics. This particular operation has parallels in the thermosetting branch of the plastics moulding industry.

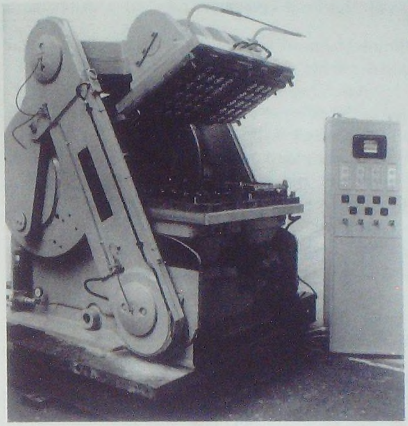


FIG. 17

GRG mechanical goods press. (*Courtesy*: Francis Shaw, Manchester.)

By continuing the exercise along the same technical course as for direct extrusion, i.e. continuous compaction, it should also be possible to feed the continuous strips via a screw linked to either an injection or transfer moulding press. Furthermore, by the design of suitable machinery it will also be possible in due course to direct injection mould from powder pre-blend.

The technology of injection and transfer moulding from a compounding angle has parallels in extrusion technology.

This is an area where considerable worldwide effort is being carried out and it goes without saying that when, ultimately, success is achieved, the rewards will be more than worth while. Already, pilot scale production has been seen in operation and to be viable (Bayer AG, Leverkusen, W. Germany).

In the injection moulding field, Bayer have shown that a horizontal injection moulding machine, fed directly with powdered rubber pre-blend via a hopper and mixer screw, can be operated fully automatically, without personnel. Such a system is also in factory quantity production.

Extrusion by Hot Feed Techniques

This is the method most widely used, and basically consists of taking matured slab rubber compound, and if hard, passing it through a cracker mill in order to warm it up. It is then fed to a rubber mill, and may be fed to the extruder by rolling 'dollies' from the mill, or in cut strips or by other automatic means.

Despite being the oldest method of extrusion, it is still perhaps the best for consistent and most rapid extrusion, although there are technologists who would argue otherwise. However, the answer is to draw one's own conclusion by experience, and then use the method which best handles the compounds in use in one's own factory. The chances are that it will be the hot feed method!

Extrusion by Cold Feed Techniques

Cold feed extruders, as the name implies are fed by cold stock which may either be in pellet, chunk, or strip form. The design of the machines in use varies considerably both in barrel diameter, screw length ratio, the shape of the flights and indeed the method of actual feeding, which can include serrated screws at the inlet end, direct feed into the screw, or slipping clutch rubber feed. The choice, or use of each of these individual systems largely depends on the type of polymer and hardness of the compound in question.

Hot Feed Versus Cold Feed

The merits of hot feeding versus the cold feeding of rubbers has long been debated, and indeed has not really been resolved because of the variance of handling properties of one compound to another. In the end it really answers itself in the factory by seeing how a particular recipe behaves. This is not too bad when there are several machines of both types available, and with the necessary production capacity. Under such circumstances, it is possible to choose the machine which gives the best results. Unfortunately, circumstances do not permit such luxury in the average rubber factory, and the poor compounder usually has to make compound changes which really should not have to be made, as more often than not, processability sacrifices physical properties.

In real terms, cold feeders are stated to possess the following advantages over hot feed machines:

(a) Less capital cost—no mills, etc.;
(b) Less labour involvement;
(c) Better temperature control of the compound;
(d) Capability of handling both low and high Mooney compounds.

If each of the above claims is closely examined, several startling facts are revealed. It is a fact that no mills are used in the vicinity of the extruder, but these are still required in the preparation areas for making strips, chunks and diced material. Mills are also required to slab-off waste extrudate, scrap in-process returns, etc. If the capital cost of all the extra equipment required is added together, the chances are that the set-up will be higher than that for hot feed.

If the cost of the labour involvement is examined the so-called saving of a mill operator, is only transferred back into the preparation areas, plus other hidden costs, and not the least of which quite often is the introduction of processing problems. Not all compounds are capable of satisfactory granulation, in that they stick together in storage. Dusting or spraying with anti-tack materials only partly solves this problem, and introduces strong possibilities of bad fusion within the extruder.

It is agreed that with machines designed very recently there is better temperature control, but this had to be introduced to take care of the high frictional heat developed, particularly with high Mooney stocks, as are found in hose making. Temperature control is certainly no problem when feeding such materials via a hot feed extruder.

Perhaps it is this final point that could well be the deciding influence in deciding on new or replacement equipment; the versatility of the cold type machine is nowhere near to that of hot feed machines, in that much tighter technical mixing control limits such as storage times and plasticity are necessary. This is particularly the case when processing some of the more specialised polymers and, on many occasions, it is necessary to have to compound to suit the machine, as well as all the actual properties and requirements of the stock. This is completely unfair and is an additional burden on the factory compounder whose job is already difficult enough.

Another fact not perhaps considered sufficiently is that the use of scrolls is not universal, and special designs are often necessary for certain so-called 'difficult' compounds. These same materials, process in the main without difficulty when fed to the extruder via a mill. Indeed, sometimes, it is necessary to feed 'cold feed' extruders with hot rubber in order to get it to process!

While on the subject of scrolls, the cold feeder types tend to wear faster and need repair or replacement more often than the hot feed types, obviously because of the extra work necessary to warm-up the material.

Pressure build-up within the head, and especially within a crosshead requires attention with high Mooney compounds, and this once again is no problem with mill fed hot compounds.

Summarising, therefore, if a mill is used for feeding the extruder, and if it can be used with careful planning to feed more than one machine simultaneously, then taking into account all of the aforesaid, there is no doubt at all which is the better system either from cost or processing angles.

One practical and fairly widely used set-up which gives the best of both worlds is to feed a small mill via a cold feed extruder, and then strip cut and feed a hot fed extruder from this mill. Excellent extrusion control is so obtained, although it could be argued that this is too luxurious for an average rubber works.

In general, the barrel/screw ratio of a hot feed extruder is approximately 8:1, and can be as low as 4:1, whereas the absolute minimum for a modern cold feed rubber extruder is ideally 14:1, and indeed machines in excess of this ratio are in widespread use in the GRG, hose, and electric cable fields, and some of these have screw designs which are eminently suitable for powdered rubbers.

Some of the current available designs of extruders include the transfer mix and the plastiscrew principles and machines Andouart, Berstoff, Farrel-Bridge (Fig. 18) Iddon (Fig. 19); Meilefer, Pirelli, Royle, Shaw, Troester, Werner & Pfleiderer, etc.

These are just some of the many machines available currently and omission of other excellent manufacturers is not intended to offend, as it is obviously impossible to list or describe all of the machines; it is hoped that those manufacturers not included will understand.

Transfer Mix

This machine can be used for dual purposes—either for continuous mixing or for extrusion. In its latter application, the design of the

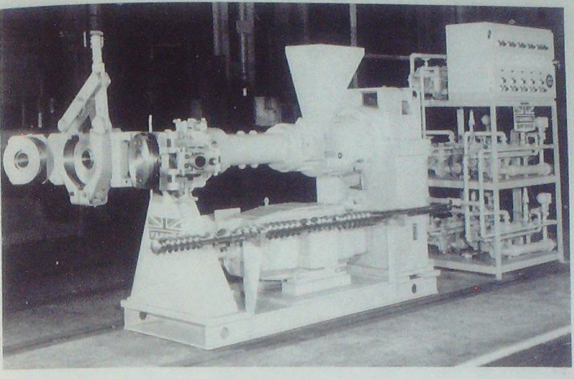


FIG. 18

Farrel-Bridge cold feed extruder. (*Courtesy*: Farrel-Bridge, Rochdale.)

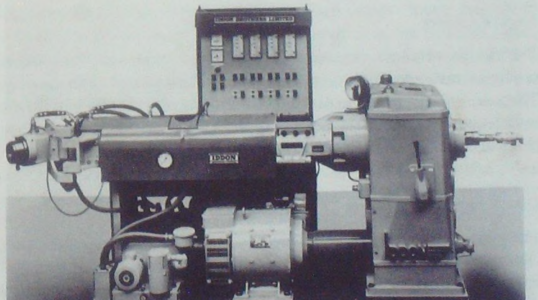


FIG. 19

Iddon cold feed extruder. (*Courtesy*: Iddon Bros, Leyland.)

screw and barrel allows the compound to pass backwards and forwards prior to final extrusion, and this ensures adequate warming-up, in the presence of water cooling, which is quite efficient.

Plastiscrew Extruder

The basic design feature of this type of extruder is in its screw. Material is fed via the throat of the extruder in the normal manner, and along the scroll, the first function of which is similar to any other conventional extruder. It then changes to a helical form, with a lead length double that of the screw flights about it. The portion nearest to the barrel forms with it a narrow aperture, through which the stock has to pass. If required, a vacuum system may be added along the barrel, thus virtually ensuring non-porous extrudates.

Pirelli Extruder

The principle of this machine is that the volume of a conical screw channel reduces progressively through the section, and an equivalent volume of stock equal to this reduction spills continuously backwards over the screw flights and towards the feed. This ensures back blending and also vigorous circulation within the screw.

Shaw Extruder

The design of these extruders incorporates three very important requirements necessary for a large volume output of high quality. These are constant feeding of the screw and a screw of sufficient length to adequately work the rubber, plus a specially balanced head (Figs. 20 and 21).

Direct Powder Extrusion

The plastics industry has been direct extruding PVC compound pre-blends for many years, but there are big differences between these and pre-blends made from powdered rubber and the compounding ingredients. The mechanism with PVC is one of gelling within the extruder, whereas with powdered rubbers tremendous heat is generated, which without control, precures, along with thermal degradation, which can be quite violent if care is not taken.

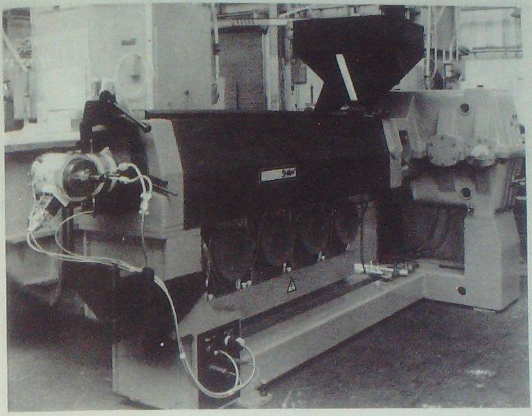


FIG. 20

Shaw cold feed extruder—new crosshead. (*Courtesy*: Francis Shaw, Manchester.)

Experiments have shown that in such cases there has been consolidation and some shear behind the dies in the extruder head, and this basic evidence has been the starting point of many workers in the field of powdered rubber, with varying degrees of success. Further to these basic facts, subsequent work has shown that if the powder pre-blend is consolidated with 'pill-making' techniques, and if the pellets so made are fed into an extruder, then satisfactory extrusion is possible with most polymers. Very good and smooth extrudates have been produced with barrel/screw ratios of as low as 12·5:1, but ideally in order to cater for most variables with powdered rubber recipes, the ratio should be at least 18:1, with or without special screw configurations as circumstances demand.

Bayer Compaction System

Having now established the fact that with consolidation of pelletised pre-blends, direct extrusion is possible, a continuous compaction

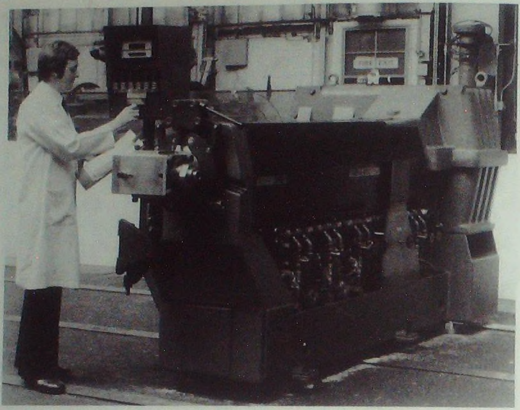


FIG. 21

Shaw cold feed extruder. (*Courtesy*: Francis Shaw, Manchester.)

technique is obviously desirable. This has been achieved and perfected by Lehnen of Bayer AG, who ascertains that the bulk density of the pre-blend was approximately 3:1, so that a compaction factor of three was decided upon for the continuous compactor. A compactor has been developed which is horizontal in format and this produces twin strips of compact pre-blend mix, in a form suitable for feeding the extruder.

Direct Powder Extruders

Parallel to the development of the compaction technique Bayer, together with extrusion manufacturers (including Berstoff (W. Germany), Farrel-Bridge (UK), Iddon (UK), Stewart-Bolling (USA), Troester (W. Germany), and Werner & Pfleiderer (W. Germany)), were also involved in various machine and screw designs.

Work showed that very high levels of dispersion are obtained by extruding powder pre-blends with or without compaction, under ideal and correct conditions, so that the physical properties so obtained are at least equal to and often better than the control compounds made from baled rubber using the same recipe.

The EVK Mixing Extruder (Werner & Pfleiderer)

The designers say that the EVK is a continuous single screw mixer/extruder, which differs from conventional deep extruders because of its specially designed mixing and kneading capabilities. The operating principle of the machine is due to the design of the screw geometry which has shearing and compound distributing sections along its whole length. This in turn rotates in a smooth cylindrical barrel.

The fact is, that maximum shearing stress is the same for each volume particle, despite the differences in distance travelled by the compound particles, and the machine can operate when only partly filled because of the shearing barriers distributed along the whole of the length of the screw.

The Mixtrumat (Stewart-Bolling)

The machine operates continuously by feeding two or more ingredients, or a pre-blend into it. The in-feed screw conveys the materials to the mixing chamber, where mixing and fluxing occurs prior to transfer to the transverse extrusion screw. Vacuum vent and forward end die are additional optional variations.

MVX Machine (Farrel-Bridge)

*M*ixing, *V*enting and e*X*truding are the designating letters of the machine's name. The machine is capable of handling pre-blends of particulates of up to at least 10 mm rubber particle size, as well as conventional powdered rubber pre-blends. Continuous venting ensures freedom of extrusion voids and porosity, and the extrusion section can be fitted with a crosshead to either direct extrude or strip extrude for feeding extruders in the conventional manner. Considerable energy savings are also possible with this technique (Fig. 22).

This machine brings the flexibility of operation of the two roll-mill and Banbury mixer into the precision extrusion of finished rubber sections, whilst reducing capital expenditure, floor space and energy usage, and at the same time improving the quality of the finished product.

The MVX is fed with particulated rubber/powder pre-blends which have been prepared in a high speed powder mixer. The pre-blend contains all the ingredients—polymer, fillers, reinforcers, softeners, accelerators and curatives, all uniformly pre-blended. (Pre-blends can be stored for months before use and allow a convenient method of storage and distribution of compounds around the factory.)

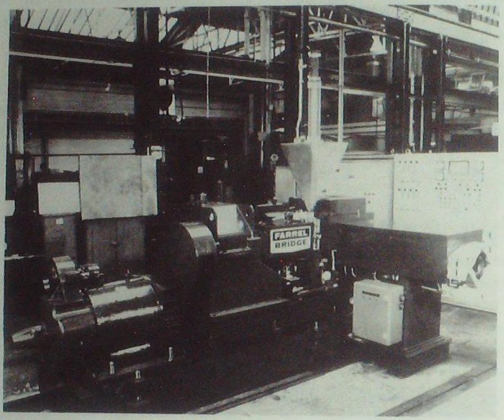


FIG. 22

MVX mixing extruder. (*Courtesy*: Farrel-Bridge, Rochdale.)

The MVX first masses this pre-blend, then mixes. During mixing, moisture and other vapours are vented to the atmosphere. After mixing, the compound is transferred, via a short passageway, to the extruder screw section. A vacuum unit removes air to ensure a porosity-free extrudate.

The MVX has two separate variable speed drive motors in order to achieve optimum conditions for both mixing and extrusion. Independent adjustment of the motor speeds enables a wide range of compounds to be processed on the same machine without changing the screw or mixing rotors.

At present two sizes of machine are available:

(a) 134/120 'Profiler' MVX—150/75 kW drive motors for outputs from 200 to 600 kg/h or extruded section. Output is dependent on the die size and formula.

(b) 240/150 'Compounder' MVX—200/75 kW drive motors for outputs of 400 to 1000 kg/h of compounded strip to feed other cold feed extruders.

The mixing section of the MVX incorporates rotors with a patented 'Delta' profile, based on the highly intensive shear, smear and blend action of the Banbury mixer.

MVX Advantages

The following advantages are justifiably claimed by the manufacturer:

continuous processing
compact size
electrical 'peak loads' considerably reduced
big savings in mixing energy
better product uniformity
improved physical properties
fully automatic operation
processes very hard compounds
'scorch time' problems eliminated
precise temperature control
clean-down time reduced
ideal for microprocessor control.

OTHER VULCANISATION PROCESSES

Hose

The vulcanisation system used in the hose industry depends very much on the type and method of manufacture. A useful comparative chart correlating cure time and saturated steam pressure is shown in Fig. 23.

It cannot be over-emphasised that consolidation, especially during vulcanisation, is of paramount importance. It is, therefore, not surprising that the systems now to be described in the main and to

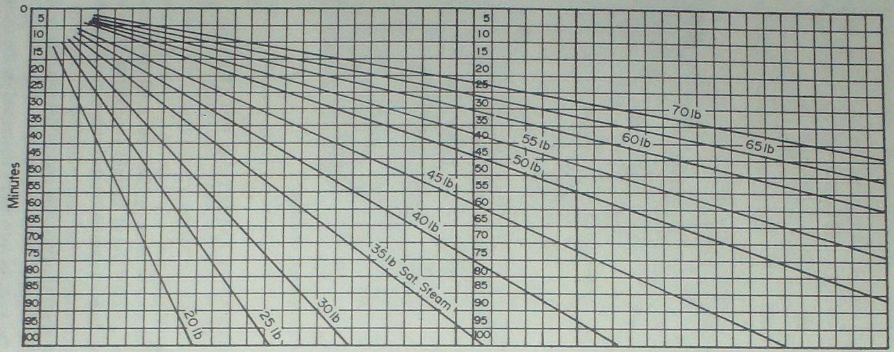


FIG. 23

Comparative cure chart. (*Courtesy*: Dunlop Ltd.)

varying degrees, embody this principle. These systems include:

(a) Moulding techniques,
(b) Consolidation by cloth wrapping,
(c) Open steam and water systems,
(d) Continuous and semi-continuous methods.

Some of these systems can be used either singly or combined.

Moulding Techniques

Moulded long length hose is one of the types manufactured by this method, and this is achieved by vulcanising under an encapsulated lead tube or sheath. It is at this stage that the hose meets the lead. A sheath of lead is made to surround the cover and this is carried out by passing either through a lead press or lead extruder (Figs. 24 and 25). (These operations will be described in detail later.) The lead sheathed hose is next wound onto a large drum. The lining is now filled with water, pressure applied, and the ends of the hose and lead are

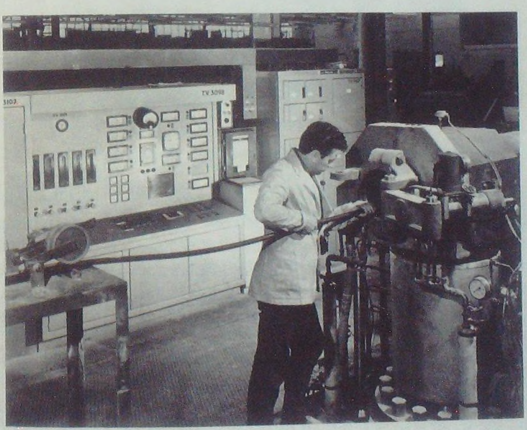


FIG. 24

Lead extruder. (*Courtesy*: Dunlop Ltd.)

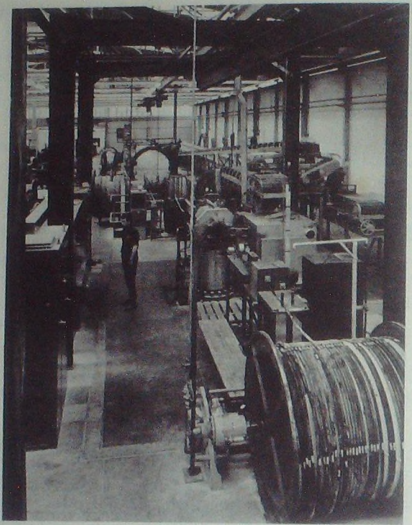


FIG. 25

Lead extruder/curing line. (*Courtesy*: Dunlop Ltd.)

clamped. The drum and contents are placed in large vulcanising pans (steam autoclaves) and curing is carried out. The water inside the hose in fact expands and becomes superheated. The hose is pressed against the lead, which acts as a mould—hence the name of the process. If the inside of the lead is fluted then such a finish is imparted onto the hose. If smooth dies are used to form the lead, then of course a smooth finish is produced.

After cure and cooling the clamps are cut from the hose, and then the lead is removed from the hose by slitting along its length in a stripping machine. The cured hose is coiled up, tested and inspected and the scrap lead is returned to the melting pot for re-use. It will, therefore, be seen that the lead is in fact circulating in a closed circuit and is thus somewhat different in usage to its part in the manufacture of electric cables where a fair percentage of lead or lead alloy is 'lost' by leaving it within the cable construction.

When manufacturing long length hose on a lead press, this circulation does not really present a problem; there can be no slippage within the press as the extrusion pressure is applied continuously by means of ram pressure. With a continuous lead extruder, i.e. whereby the lead is extruded by means of a screw or scroll, it has been found that much cleaner and chemically pure lead is needed. Indeed, it is necessary to keep this cleaning and purging operation under tight laboratory control.

Control of Lead Quality

Investigation has shown that initially virgin metal of 99·997 % purity is best and should be very low indeed in copper and bismuth content. Due to recirculation inherent in the process, however, contamination of the metal occurs in at least three ways.

(a) By the action of steam on the lead-producing hydroxide, which in turn becomes oxide in the melting pot.

$$Pb + 2H_2O \rightarrow Pb(OH)_2 + H_2$$
$$Pb(OH)_2 \rightarrow PbO + H_2O$$

(b) By the action of the sulphur in the rubber compound reacting at the inner lead surface.

$$Pb + S \rightarrow PbS$$

This is partially soluble in hot molten lead.

(c) By the usual action of the atmosphere on the surface of the molten lead in the melting pot.

$$2Pb + O_2 \rightarrow 2PbO$$

The formation of lead oxide (dross) is not new, and much work has been done on this aspect of contamination. Indeed, there are many theories as to whether or not the dross should be totally removed from the surface of the melting pots. However, several successful ways and combinations of the following systems have proved to be of practical use in various parts of the world.

1. The use of two melting pots, which gives better separation of dross.

(2) Treatment of the lead by stirring in a carbon/ammonium chloride mixture. This reduces the dross chemically and the ammonium chloride helps to flux the system.

$$2PbO + C \rightarrow 2Pb + CO_2$$

(3) Gas heating for melting the metal which gives a reducing atmosphere across the surface of the metal.
(4) Nitrogen gas which when bubbled through the lead purges well.
(5) Rather amusing, but nevertheless scientifically explainable, 'arts' seen in operation include the addition of sawdust, onions and potatoes to the lead pots.
(6) Correct temperature control of the particular melting system.
(7) The use of carbon dioxide in the autoclave during vulcanisation.

All the comments referring to dross, apply equally well to a press and/or continuous extruder, but unfortunately the problem of lead sulphide applies only to the screw extruder, in that this contaminant deposits on the scroll and after a time causes surges in the extrusion and gradual fall-off in weight delivery performances. Ultimately it becomes necessary to strip the machine and clean the screw. The time between clean-down may be lengthened by several methods as described below.

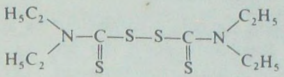
(a) The treatment of the lead by the addition of a controlled amount of sodium. This can act as a dual purpose system helping to remove both oxygen and sulphide simultaneously.

$$PbO + 2Na \rightarrow Pb + Na_2O$$

$$PbS + 2Na \rightarrow Pb + Na_2S$$

(b) The cover compound vulcanising system may be changed to what is known as a 'low sulphur' or 'sulphurless' one. Normally a hose cover compound contains some 2·5–3% of added, elemental sulphur—one of 'low sulphur' can include accelerators of the thiuram type with either very small amounts of sulphur (0·3%) or, if economics allow, total replacement of elemental sulphur in such a system by either elemental selenium or tellurium. These latter two elements form lead selenide and/or lead telluride which have less tendency to adhere to the scroll than lead sulphide.

With the thiuram system, the sulphur is not 'free' but in amounts which can be liberated under control.



Tetraethylthiuram disulphide

This liberation of sulphur is just sufficient to vulcanise the polymer, without leaving much free sulphur to react with the lead—hence cleaner lead.

Press Moulding

Another widely used system is to cure in a long mould contained within a conventional bed press as is used in the conveyor belting industry.

The mould usually consists of a series of parallel and hemispherical grooves, running the length of the press. They can be virtually any length, depending obviously on the length of the press. Presses have been seen in use as long as 40 m (130 ft), and the hoses are mould cured by a stop and repeat principle, in lengths up to 250 m (820 ft), depending on bore size and total weight of the length.

This process is ideal for small bore sized hoses, especially welding industry types, and also certain types of hydraulic hose which are made this way in Germany.

Twin weld hose of a very high quality is also manufactured in the USA by this method. The specification covering this hose calls for a very high and strong web strength between and joining the two hoses together (oxygen and acetylene) so that they are not torn apart in service. This method is claimed to be the best.

Convoluted Moulding

Hose shapes especially of the convoluted type are usually made in discrete, short lengths by moulding an extruded tube (with or without a fabric interply), between metal formers. Provision is usually made for the application of a low negative pressure, during vulcanisation, to assist the forming operation.

Consolidation by Cloth Wrapping

(i) Straight wrapping for cure is carried out by applying a broad wrapping cloth lengthways down the unvulcanised hose, and consolidating in a three-roll wrapping machine. The cloths which may be of fine nylon, linen and/or cotton, or mixtures are usually applied damp, so that deliberate and controlled shrinkage can occur during the cure cycle. This shrinkage of course then consolidates the hose parts into an integral and homogeneous whole during cure.

(ii) Spiral wrapping, as its name implies, encloses the uncured hose in narrow and long cloth strips, applied spirally either in a conventional three-roll wrapping machine or from a taping head revolving around the hose, in a sun and planet pattern. It is normal practice to wrap with a 50 % cloth overlap, which in effect applies two layers of cloth in one operation. Once again the cloths are damped for shrinkage to consolidate, and can be of nylon, linen, cotton and/or a mixture of these textiles. Of course other fibres can be used, but the ones mentioned are the most widely used.

Open Steam and Water Curing Systems

Both of these systems are used mainly for the lower pressure rated mechanicals and hoses, where minimal consolidation is needed for satisfactory use in service. The systems used are variations of a theme in that either a flexible mandrel may be used, or the hose filled with water and the ends sealed, or even left open. The uncured extrudate is coiled on to trays, in single layers, and separately stacked one on top of the other, rather like a gramophone disc magazine. Ideally they are then placed into a vertical rather than a horizontal autoclave and the autoclave closed. Steam is then very rapidly applied and the vulcanisation completed for the prescribed cycle. The pan is then cooled while still under pressure, otherwise blistering of the cover can occur.

In the so-called 'water' cure, the pan after loading with the hose, is filled with cold water and then the steam is applied and the cycle finished off as above.

CONTINUOUS AND SEMI-CONTINUOUS METHODS

Cables

Steam Tube Vulcanisation

The continuous vulcanisation process used within the electric cable industry has been in use for many years and is a proven one. Indeed it has been developed to a fine art and has become so sophisticated that its use has been put to specific sizes of types of cable. Basically the process consists of a long steel tube attached to a crosshead extruder. Either insulation or sheath may be applied by the extruder depending on the type. The cable passes from the extruder into the steel tube which contains high temperature and high pressure steam. The steam is contained within the tube by a telescopic seal at the extruder end, and either rubber or water seals at the other end. The length of the tube and hence the cure, is determined by the line speed of the cable, together with the pressure and temperature of the steam in it. It is usual for a tube to be around 75 m (250 ft) in length, but this obviously depends upon local and environmental circumstances.

The early tubes developed were basically horizontal, and many are still in operation. However, this system has cable size or rather cable weight restrictions around the 0·23 kg (0·5 lb) per foot mark, in that if this weight is exceeded, the cable is dragged along the tube bottom, with disastrous abrasion results. To overcome this, vertical tubes were developed and introduced. This necessitated the building of high towers, and installing the extruder on a platform, at the top of the tube, so as to extrude vertically downwards and into the tube.

Following this the catenary system was brought into use, as a part compromise, particularly from a plant cost and installation angle. In this system, the extruder is mounted on an elevated platform somewhere in the roof of the building, and the tube has a curvature over a distance of approximately 18–24 m (60–80 ft), or even longer, depending on the weight and size of the cable, and of course the tube length. This tube curvature enables the cable to take its natural curve (due to weight) when passing through the tube and without touching the early and critical stage of vulcanisation. It does not then matter, within reason, if the cable does touch the tube bottom along the horizontal portion, as an adequately vulcanised skin has already been formed.

It is thus seen that any of these three tube methods is an extremely efficient way of vulcanising an electric cable, but it goes without saying that extremely long runs are necessary for economical reasons, as valuable time is lost in set-ups on only a short run. Indeed, in a well planned factory, short runs are not considered. These are taken care of by the already well known and earlier established cable making techniques.

Thus, it can be seen that one or other of these processes could well have possibilities for the continuous vulcanisation of the fairly recently developed long length flexible mandrel hydraulic hose process, and indeed this is the case, as the system is already in use. Once again, long runs are very desirable.

The main differences of course between cable and hoses in this method of cure are that the rubber compounds for hose have to be cured tighter, and in addition to insulation or cover in a cable, the lining and cover have to be cured simultaneously in a hose. This necessitates very special and difficult compounding techniques. Very recently a system has been introduced in which the steam has been replaced by pressurised hot air or inert gas under high velocity.

FIG. 26

PLCV curing system. (*Courtesy*: General Engineering Ltd.)

Pressurised Liquid Continuous Vulcanisation (PLCV)

A pressurised LCM version has been developed and proved to be satisfactory under production conditions for the manufacture of electric cables.

This consists of a straight tube, installed at a slight angle, but not incorporating a catenary. The tube is pressurised with air or inert gas at the extruder end, and the cable passes through this into the molten salt. The engineering design ensures that the molten salt and the pressurised water and seal at the outlet end are separated.

Advantages of this system are that unlike steam tube curing, the vulcanisation temperature is independent of the system pressure, and this pressure can be applied completely independently of the temperature.

A catenary is not necessary due to the buoyancy support given to the cable because of the specific gravity of the molten salt (Fig. 26). Additionally, touching of the walls of the tube with uncured material is not as critical as with the straight steam tube techniques.

GENERAL MECHANICALS

Microwave Curing

This system has application in the extruding industry and low pressure applications within the hose industry. The use of microwave curing within the hose industry is generally speaking limited to non-metallic hoses because of the metallic interference. However, investigation is currently being carried out by some plant manufacturers in this latter respect. Because of the limitation, coupled with the necessary use of crosshead extruders, high plasticity compounds and consolidation of the reinforcement portions of a hose, it is considered that within the hose industry only processes involving plain tubing and low pressure service applications such as garden and automotive heater hoses, etc., will be or are viable.

In this connection microwave curing is neither better nor worse than LCM and fluidised bed techniques, but it does have advantages over the latter two when it comes to cleanliness. The heating is far more uniform throughout and there is no need for the latter cleansing operations of either the LCM salt or fluid bed balotini (sand-like material). It is, therefore, very suitable for the continuous production of mechanical rubber goods.

Fluidised Bed

In this system, the vulcanisation chamber or trough contains a bed of heated fluidised particles, through which continuous extruded rubber sections may be easily passed without resistance. The bed of particles of balotini, a sand-like material, is heated by electricity and the balotini is fluidised by passing air or superheated steam through it. Operating temperatures of up to 240 °C (464 °F) may be obtained, thus making possible an extremely short curing cycle. Of course, the length of the bed unit is quite easily varied to suit specific manufacturing conditions, and the temperature may also be varied accordingly.

To prevent porosity of the compounds when vulcanised at these high temperatures, caloxal may be added during the mixing stages of the stocks. This curing process is ideal for continuously extruded sections, and continuous hose lines have also been developed using this system. Currently only comparatively low pressure hose, such as garden or car heater hoses and extrusions, are in production owing to the fact that consolidation cannot be achieved in open fluidised beds. However, production development is well advanced in several countries for a pressurised bed, which incorporates a special water seal and this enables the pressure to be retained without a mechanical seal. This should enable hoses of even higher pressure ratings to be vulcanised by this method, and it will be interesting to see how far this can be achieved while still retaining the high line speeds necessary for economical hose production.

Liquid Curing Media

This process is also known as salt bath curing, as special easily meltable salts are used in the vulcanisation trough. These consist of various ratios and mixtures of salts of sodium and potassium usually nitrates and nitrites and vary according to the proprietary brands available and also the wishes of the factory compounder concerned. The process is extremely efficient and is fairly widely used, once again for extruded plain tubing and low pressure hose. A salt bath may also be used in conjunction with a continuous lead extruder for certain higher pressure types of long length hoses.

Safety and fire precautions are obviously needed and are indeed quite stringent for operation of LCM systems, and a further disadvantage is the necessary removal of excess salt by washing in water after vulcanisation.

Helicure Process (Du Pont)

This is another extremely interesting process, and is suitable for tubing, low pressure hose, mechanicals and similar materials. This process consists of extruding the hose or tubing into a helical and vertical coil, containing hot circulating fluid. The extrudate is carried along by the velocity of the fluid, and the length of the coil and temperature of the fluid ultimately determine the state of cure. This process is suitable, however, only for the lower pressure types of hoses, where applied pressure is of little importance.

CHAPTER 5

TESTING AND QUALITY ASSURANCE

Statistics can be used extensively in most manufacture as a method of quality control, and have proved extremely valuable. The rubber industry is no exception to this. A confidence level of 3% is recommended, which includes the testing errors. Random sampling and control charts of mean values may be used both as a control over the intermediate stages of the processes and also to check the finished product.

The amount of statistical testing of the end product depends upon what it is. Products which are easier to make and where failure is fairly unimportant, such as say lengths of low-pressure garden hose, are infrequently tested for 'burst'. Other materials which are more difficult to make are tested more often. Yet for aircraft components, where there is no margin for error, statistical checking is not used at all—each item must be tested or checked individually.

The control chart method may also be used for the analysis of experimental results and in the experimental investigation of new compounds.

MATERIAL TESTING

It is suggested that the main testing is of the material as it comes off the mill. Each batch is sampled and tested for plasticity, using the Wallace Rapid Plastimeter, Mooney or Rheometer, and for correct specific gravity, using say, the L'Homme and Argy balance. Borderline specific gravities are remeasured, using an accurate balance and the weighing in and out of water method. A portion of the sample may be cured in an open pan or press, depending on the curing procedure in the manufacturing process, and hardness measured with a Wallace Rapid Hardness meter and the results plotted. The control charts afford a visual check on the processes, and it is easily possible to detect anomalies and take curative action in time.

The rubbers are also checked for moisture and ash. It is found that checking the Banbury or mill outputs in this way gives a very good control over the extrusion properties of the material. The measurement of specific gravity as a check on compounding accuracy is quite satisfactory when the specific gravity is measured within ±0·02. Fillers are tested for moisture, manganese, copper and iron content. Accelerators and antioxidants are checked by moisture content and melting points.

The control charts are constructed with the two control lines at the 3% position, and control lines for instrument errors are also included. All the testing instruments are themselves tested and their errors are evaluated for setting up control limits. The variation in results between different assistants using the same instruments should also be investigated—this is of particular importance in hardness testing. Even in the use of micrometers it is important to check the errors; the same operator should do all the measurements. Changing of operators has been shown to cause discrepancies of up to 0·18 mm (0·007 in) on a hand micrometer.

In general the widest possible control limits should be used that will meet the specification; control limits should not be set just for their own sake. All control tests must have a real meaning with reference to the process they are controlling. Technological progress and the increasing emphasis on improved manufacturing tolerance over the years have brought about a rapid development of the techniques of quality control, making it virtually a new industry in itself.

Process/Quality control can conveniently be divided into five sections: (a) Pre-production control of raw material; (b) control of basic ingredients and components made up from these raw materials; (c) control of physical manufacture; (d) control of curing or processing; and (e) final checking of the completed product.

Right at the beginning, all types of rubber compounding ingredients must be rigidly controlled as they reach the factory, in terms of a specification agreed with the supplier. Further tests need to be applied while the rubber is being compounded and the product manufactured. When manufacture is complete the finished material must be examined, care being taken that the tests applied bear a sensible relation to the service any particular article is required to give. Nevertheless, this is not the end as far as the test organisation is concerned. It is most important that test results are correctly interpreted. That is to say the significance of the figures must be known in relation to any margin of error, so as to avoid drawing conclusions which are too optimistic, or taking rash decisions on a few unrelated figures which might result in a serious dislocation of production. This calls for a statistical approach to the problem, so that the final decision is soundly based.

RUBBER BLENDING

Rubber blending begins with tests on crude rubber, particularly in the case of natural rubber. The man-made product, being itself produced under closely controlled conditions in a chemical factory, can usually be relied upon to meet a specification within set tolerances. On the other hand, the natural product, coming as it does from different trees grown on different soils and subject to local variations, cannot be expected to have the same uniformity. Rubber growers have made great strides towards a more effective control of certain essential properties, such as speed of vulcanisation and workability, but it is still desirable to blend incoming lots to mix thoroughly deliveries from different estates.

Ingredients for compounding with the rubber usually come from the suppliers with a test report, but if not, tests are carried out in a factory control laboratory. This should be well equipped with both standardised and specialist instruments for chemical and physical tests. In the case of cured rubbers, tests are carried out for moisture and ash. For compounding ingredients, the tests include microscopic ones on the size and shape of particles, moisture content, metallic impurities for certain ingredients and melting points for others.

Usually, no raw materials are released for manufacture until the control laboratory is entirely satisfied and has issued a certificate. With many large firms this type of laboratory is approved by AID and other Ministry Departments. Additionally, procedures as per Ministry of Defence 05/24, etc. may be used.

Control normally starts with the admission of raw materials to stores. Where no certificate of purity is issued by the manufacturer with his materials, or where there may be reason to suspect contamination during delivery, it must not be released from the stores for production unless tests prove it satisfactory. This procedure applies to all incoming raw materials. There will be a number of basic rubber compounds, both natural and synthetic, plus the usual 'accessory' compounding ingredients, including carbon black, sulphur, accelerators and antioxidants.

To ensure that a high percentage of output falls within the product specification, the manufacture of both rubber and plastics products must be carried out under close supervision. This is particularly important in the case of compound manufacture and it is complicated by the fact that there are a very large number of different compounds to consider, perhaps not far short of a hundred in a large production unit. The compound and process instructions for making it are usually recorded on a readily available card, and it is the function of a process control laboratory to see that these instructions are carried out. To this end technical officers are attached to the production department to watch for any signs of approaching difficulties. They ensure that samples of all compounds made are systematically passed back to the laboratory for tests on processability in the subsequent shaping operations, together with physical tests on the properties after vulcanisation. As in the case of the separate materials, mixed rubber compounds will only be released for the next stage in manufacture when the control laboratory has certified their quality.

FLEXIBLE SYSTEM

A control system which is sufficiently precise but which retains the necessary flexibility to cope with complex production utilises progress cards. A card is issued for each scheduled production item and must accompany this item through every stage of manufacture. Production is so arranged that no stage or process can proceed until an experienced technical inspector is satisfied, first that the preceding operation was correct, and second that the operator has clear instructions and the appropriate materials for the next stage. Where the stage in question is a continuous run such as extrusion or calendering, the equipment should be stopped for a technical check near the commencement of a run, after a few feet have been produced, to allow for initial stabilisation. If this procedure is rigidly enforced and the operatives made to appreciate its practical value, the production process becomes much more effective and reliable.

At no staff level, however, can the human fallibility factor be ignored. Even if it were possible, control systems organised and instrumented to exclude this factor could well be uneconomic, but steps can be taken to reduce the probability of human error. If production data or test results can be automatically presented in graphic form, the necessity for working with large numbers of similar figures can often be removed. The progressive picture presented by a graph facilitates the early detection of deviationary trends in a process, enabling correction to be applied before specification limits are reached—a question of prevention rather than cure.

Approved compounds next pass through the various processing operations such as extrusion, calendering, moulding and vulcanisation. These are supervised by patrolling inspectors, to ensure that the process is being correctly followed and to solve any production problem that might affect the quality of the final product. Special care is taken with continuous processes such as extrusion and vulcanisation to make a thorough check of the conditions at the start of a run, followed by periodical checks to ensure that no variations take place during the run. It is often the practice for each run to be metered by a production card, which is initialled at suitable stages by the officials concerned, to ensure that production continues according to specification.

The culmination of all raw material and manufacturing control will be seen in the finished product, and it is of primary importance that this shall be so tested as to leave no doubt that bulk production can be relied upon to meet specifications. The tests applied vary considerably, according to characteristics and service requirements of the product and are usually specified in the appropriate British or International Standard.

SERVICE SIMULATION

With such a wide range of properties the types of product testing called for are very diverse. In addition to straightforward tensile, elongation, ageing and other tests on the basic rubber or plastics material, the physical properties of the reinforcing material if any must also be checked. However, the most important tests are probably those which simulate service conditions on the finished product.

Where an article has to meet solvents, its resistance to the swelling action of the solvent must be known within certain limits. Where the material handled is corrosive, resistance to the acid or alkali concerned must also be verified. Such properties are checked by examining the character of the product after service conditions have been simulated, not only by examining the internal or external surface conditions and appearance, but also by dismembering the article to check how service conditions have affected the bonding between component parts.

The process control problem is one which 'snowballs'. A large number of basic ingredients beget an even larger number of working compounds which, in turn, are used in a still greater number of different types of products. Providing care is taken to ensure that all staff do appreciate the very real benefits of quality control systems, they provide the best possible insurance against production loss due to natural manufacturing variations. However accurate are the tests of raw materials, factory processing or finished product, they are of little value unless correctly interpreted. With each test the probable margin of error must be known. This tells the control staff just how significant is the information they get from instrument readings and enables them to take the right decision about their future action.

FOLLOW UP

This now leads in to the 'follow up' procedure necessary to ensure that once the system has become established and accepted, it continues to do so. This of course does not happen without effort. Every action must be monitored, followed up and recorded. At set periods certain actions must be checked, rechecked *and recorded* to ensure that these key actions are indeed functioning. This particularly applies to calibration instruments, so that items such as micrometers, pressure gauges, thermometers and temperature recorders, etc. are very regularly serviced and checked. If such fundamentals were not correct, then inevitably disaster will occur.

CONSUMER DETERMINATES

Many organisations in addition to Ministry Departments, who operate QA schemes, such as the old AID, (now replaced by MOD

05/24, etc.), BS 5750, also have their own procedures. In general these are based mainly on the old systems, and in practice include 'on the spot' and 'in plant' inspections to ensure that the laid down procedures, follow ups, recording and actions taken, are in fact in line with QA manual procedures, for the manufacturing area in question. In this latter connection it is essential that the process details correspond *exactly* with the plant operations, and that from time to time, as changes (minor as well as major) become necessary, they are recorded and notified to all concerned, and be seen to be so, *by signature*. In such a short summary as this, it is only possible to highlight key areas, but it is strongly advised that reference should be made to the documents referred to above.

GENERAL MATTERS

Frequently, in factories all over the world, and not necessarily rubber factories, questions concerning the management's attitude (particularly with regard to piecework/quality bonuses, and the need for supervision) are being asked. Whose fault is it? Should the worker be blamed?

These are all very difficult questions to answer, and vary of course depending on circumstances. If the process and compounds are basically correct, and the operations are known to be under control; then if something has gone wrong, it is fairly safe to say that somewhere the human element is at fault. This is one good reason why quality control is necessary, as somebody has not in fact done their job. This, however, can in turn create even worse quality problems. If true mass or continuous production could be introduced on a wider scale into the rubber industry, then it becomes a fact that the incentive for higher outputs and productivity, does not necessarily mean more quality problems. At long last there are signs that greater mechanisation, with the removal of human fallibility, is now taking place. The blame attached to the worker or the quality man, who may not have picked up the fault quickly enough (the other half of the joint effort) is thus removed. This is as it should be, since in the vast majority of cases, nobody sets out deliberately to make or accept scrap, waste, or faulty products.

Because of conflicting interests, another very controversial matter, is to whom shall the process control, quality control/assurance, and inspection departments head? For obvious reasons, irrespective of to whom they are responsible, it is essential that harmonious relations should exist not only between themselves, but also with the production departments.

Without wishing to appear biased or too parochial, but having had personal experience of operating both types of system, and seen them operating in various plants worldwide, the best and considered correct, is for the various functions to be channeled to the Technical Director, who not only is in a neutral position (i.e. not being directly involved or responsible for direct quantities of output) but is also in a better position to pass judgement, because of his technical background. Perhaps the exception to this, is in areas where the factory and works management have had many years of basic technical works practice before becoming involved in production matters.

This reasoning has been endorsed by the ministry systems over many years. Indeed, it still is, in that the person responsible for quality must not be in contact with anybody directly responsible for production. Thus, any possibility of bias is removed, an absolute and obvious necessity in the case of say aircraft, or safety critical parts.

STATISTICAL SIGNIFICANCE

The statistical method may be extensively used and gives valuable results. The number of tests carried out with regard to any one property is determined partly by the accuracy of the test and partly by the significance of the test in relation to the performance of the hose. It is important that all control tests have a real meaning in reference to the process they are controlling. That is to say no property should be controlled more closely than is required by service conditions, but when these have determined the limits, the control system should ensure a long, trouble free run well within these limits.

It is therefore valuable to express test results in chart form and keep the charts in continuous review. An efficient control system, with up-to-the-minute results displayed in graphical form, will do a lot more than indicate that a certain batch of material is outside specification and has to be scrapped. If the results are correctly interpreted with regard to their statistical significance and clearly expressed in chart form, they will give ample warning of 'trends' in production conditions, so that corrective action can be taken long before the end of product has begun to stray over the limit lines.

Testing rubber and plastics products over the entire range demands a logical system for testing raw materials, factory processing and the finished product. The testing equipment should be first class, effectively installed in a good working situation and operated by experienced staff who fully appreciate the significance of the work they are doing. If the results obtained are understood correctly and the appropriate action taken, effective testing and control leads to smoother production and inspires the entire organisation with confidence that the end product will fully meet service requirements.

Standard Test Procedures

A procedure has been internationally accepted by ISO, based on work carried out within ASTM (USA) BSI (UK) AFNOR (France) and other member bodies where standard test recipes have been agreed. Thus minimum requirements should be met for each of the rubbers under examination. The recipes are extremely useful controls for factory acceptance of bulk deliveries of the various rubbers and carbon blacks. Other compounding materials are currently being discussed within ISO.

The procedures specify the order and time for the addition of ingredients, and also the type of mixing equipment used. These are clearly detailed in the relevant ISO or ASTM standard, and for convenience a listing of these follows. (Acknowledgement is made to ISO and ASTM for the relevant extractions and references.)

STANDARD RUBBER RECIPES AND METHODS

ASTM Reference	*ISO Reference*	
D 3182	2393	Rubber test mixes, preparation, mixing and vulcanisation. Equipment and procedures.
D 3184	2303	Rubber—Evaluation of natural rubber (NR)
D 3185	2322	Rubber—Evaluation of SBR
D 3186	—	Rubber—Evaluation of SBR mixed with carbon black

D 3187	—	Rubber—Evaluation of NBR
D 3188	2302	Rubber—Evaluation of IIR
D 3189	2476	Rubber—Evaluation of BR
D 3190	2475	Rubber—Evaluation of CR
D 3191	3257	Carbon black in SBR
D 3192	—	Carbon black in NR

Evaluation of NR (D 3184)

NR standard formula	*Reference*	
	1A *(GUM)*	*2A* *(black filled)*
NR	100·00	100·00
Zinc oxide	6·00	5·00
Sulphur	3·50	2·25
Stearic acid	0·50	2·00
Oil furnace black	—	35·00
MBT	0·50	—
TBBS	—	0·70
	110·50	144·95

Evaluation of SBR (D 3185)

	Reference	
	1A	*2A*
SBR or masterbatch	100·00	100·00
Zinc oxide	3·00	3·00
Sulphur	1·75	1·75
Stearic acid	1·00	1·00
Oil furnace black	50·00	35·00
TBBS	1·00	1·00
	156·75	141·75

Reference 1A applies to general purpose non-pigmented rubbers. Reference 2A applies to the partially crosslinked and high-Mooney rubbers.

For Oil Masterbatch Types

	Reference				
	1B	*2B*	*3B*	*4B*	*5B*
Masterbatch	125·00	137·50	150·00	162·50	175·00
Zinc oxide	3·00	3·00	3·00	3·00	3·00
Sulphur	1·75	1·75	1·75	1·75	1·75
Stearic acid	1·00	1·00	1·00	1·00	1·00
Oil furnace black	62·50	68·75	75·00	81·25	87·50
TBBS	1·25	1·38	1·50	1·63	1·75
	194·50	213·38	232·50	251·13	270·00

Masterbatch parts of oil for reference—1B = 25, 2B = 37·5, 3B = 50, 4B = 62·5 and 5B = 75.

Evaluation of SBR with Carbon Black or Carbon Black and Oil (D 3186)

Masterbatch	100·00 + X + Y
Zinc oxide	3·00
Sulphur	1·75
Stearic acid	1·50
TBBS	1·25
	107·50 + X + Y

X—Parts carbon black per 100 parts base polymer and Y—Parts oil per 100 parts base polymer

Evaluation of NBR (D 3187)

NBR standard formula	
NBR	100·00
Zinc oxide	3·00
Sulphur	1·50
Stearic acid	1·00
Oil furnace black	40·00
TBBS	0·70
	146·20

Evaluation of IIR (D 3188)

IIR	100·00
Zinc oxide	3·00
Sulphur	1·75
Stearic acid	1·00
Oil furnace black	50·00
TMTD	1·00
	156·75

Evaluation of Solution BR (D 3189)

BR standard formula	
BR	100·00
Zinc oxide	3·00
Sulphur	1·50
Stearic acid	2·00
Oil furnace black	60·00
TBBS	0·90
ASTM (103) petroleum oil	15·00
	182·40

Evaluation of General Purpose CR (D 3190)

	Sulphur modified		*Mercaptan modified*	
CR	100·00	100·00	100·00	100·00
Stearic acid	0·50	0·50	—	—
Phenyl-beta-naphthylamine	—	—	1·00	1·00
Magnesium oxide	4·00	4·00	4·00	4·00
SRF black	—	30·00	—	30·00
Zinc oxide	5·00	5·00	5·00	5·00
2-mercaptoimidazoline	—	—	0·35	0·35
	109·50	139·50	110·35	140·35

Carbon Black in SBR (D 3191)

SBR 1500	100·00
Zinc oxide	3·00
Sulphur	1·75
Stearic acid	1·00
Carbon black	50·00
TBBS	1·00
	156·75

Carbon Black in NR (D 3192)

NR	100·00
Stearic acid	3·00
Zinc oxide	5·00
Benzothiazyl disulphide	0·60
Sulphur	2·50
Carbon black	50·00
	161·10

CHAPTER 6

TECHNICAL TROUBLE SHOOTING AND PROCESS CONTROL

This chapter is written in general from a technical angle and covers the various roles played by the technical department in attempting to ensure that production is as trouble free as possible.

Initially and of paramount importance, it goes without saying that the process must be correct (and agreed as such by production). It should also contain as many built in safeguards as are technically sound, so as to take care of the human element content of the operations. Ideally as much mechanisation as is consistent with economics should be built into the various operations, thus keeping the process as automatic as possible. This could well appear to be aiming at utopian conditions, which of course are never possible within a rubber factory, but nevertheless, there is certainly no harm in attempting to reach this goal.

Many operations such as mixing, calendering, extruding, etc., are common to all branches of the dry rubber industry, irrespective of product, so where better to start the trouble shoot than in the mill room area. It is an established fact that if consistency from the mixing room can be achieved the majority of processing problems in the factory will disappear.

It cannot be over emphasised that a compound should not only be designed for its physical and other properties, at of course the right cost level, but *it must be capable of processing with the minimum of problems through the various subsequent factory operations*, and this applies particularly to scorch characteristics. If a compound shows scorchiness during the early stages of its design, it should be rejected and development work recommended. It is asking for trouble and totally unfair to expect the factory to run such a stock. Having said this, it is not always possible to eliminate this problem in a formulation that sometimes has opposite property requirements necessary to meet a certain specification. When these conditions exist, the specification should if possible be altered in co-operation with the marketing department and/or customer, and these anomalies sorted out diplomatically. If agreement cannot be reached, then it should be very carefully considered whether or not to accept the job, or at least build in a high scrap rate into the cost. If high production is necessary, then even this latter point is certainly *not* recommended, as there will certainly be regrets later.

The point has now been made that a good and as easily processable a compound as possible should be used. Having accepted this, it goes without saying that batch to batch consistency is the next important thing, and this is of course achieved by correct cycling times during the various mixing operations, and also by the use of consistent raw materials and drugs. These should be clearly defined in agreed purchasing specifications, which should also be realistic rather than theoretical. Important points should include maximum moisture content and particle size for fillers, and also cleanliness within the rubbers. Other specific requirements such as manganese, copper and iron contamination depend of course on the polymer being used and branch of the rubber industry concerned. That is why the point was made that the purchasing specification should be realistic rather than theoretical. It is nevertheless time wasteful and expensive to test for non-relevant properties. Having therefore decided that the raw materials are now consistent, regular testing either on a 100% or a statistical basis should be instituted. Another system is to have an arrangement with the supplier to submit a testing certificate with each batch of material, and having set up mutual confidence, only spot testing is then necessary. Time, experience and subsequent events show just what is necessary to achieve the objective.

Having thus now obtained both satisfactory raw materials and a recipe that is fairly scorch free, full scale trials on factory equipment are now necessary before full release to the factory. It is always necessary to do this, despite the fact that it may appear tedious. Many points are thrown up in the factory that are not always apparent in the laboratory, and thus future troubles that certainly could occur are eliminated before they even happen. Quite often it is possible to cut out the laboratory operations altogether and to mix directly in the factory. Another point to remember also is that an allowance of at least 10% fall off in properties such as tensile, elongation, etc. should be allowed between the laboratory and factory results, because factory dispersion of the compounding ingredients is very rarely in line with laboratory equipment. This however does not apply to powdered rubber pre-blends, where full physicals are developed, because of the better dispersion which is achieved.[1] (See also Chapter 3.)

Correct mixing cycles must be installed and checked regularly by process and quality control techniques. Furthermore, it is highly desirable for the internal mixer to be working on at least semi-automatic, and preferably automatic time/temperature control cycles, thus making them independent of the operators. Cooling water must also be under constant surveillance. With production requirements high, it is only human nature sometimes to cut or round off corners. With a process already designed to allow for only a minimum of this, because of production requirements, disaster is inevitable if this is allowed to go unchecked. Not only can dispersion be very variable, but more important the compound will be very 'nervy', which presents serious problems in later processing operations. If such conditions are ever encountered, the temptation to alter the compound must be strongly resisted once a certain compound has been established and given satisfactory service over hundreds and thousands of batches. When trouble is encountered suddenly, it is fairly certain that something has gone wrong in the mill room, and in particular with the mastication cycle (raw materials should also be checked). In other words, the troublesome batches should be quarantined and very closely supervised batches prepared in the mill room. It is a remarkable fact that in 99 % of such cases, the troubles will be rectified! It is also another strange fact that many of the troubles tend to occur on the night shift, and round the clock process and quality control are absolutely essential, despite the added cost. It is indeed more costly not to cover for this.

An example of this many years ago proves the point—severe nerviness of a fairly high hydrocarbon stock was experienced on the calenders with a compound that had been trouble free over a long period of time. The faulty material was traced back to the night shift, and a spot check at midnight caught one of the operatives red handed cutting the mastication cycles. The necessary action was then taken, unfortunately rather late!

Some troubles experienced in the factory are unfortunately on occasions self-inflicted and usually occur in the name of higher output or productivity. One way to achieve these latter two in the mill room is to incorporate the curatives and accelerators within the actual internal mixing cycle, rather than within the after milling process. This obviously increases the scorch risk, and a compromise is usually struck in the mixing procedure. If however trouble is experienced later, it is no use blaming the compound (an all too frequent occurrence over the years)—there is only one answer, which is to cut out the practice, as it is not technically sound anyway.

Speaking of productivity, there was an instance of a so-called outside productivity expert, who advised that considerably more output could be obtained from the mills (100% more in fact), if the rubber was banded on both rolls at the same time, instead of only using one! He genuinely believed that the roller mills were only 50% utilised! The moral here is, as always, be prepared to listen, *but* beware of pseudo experts, as these can also be present in rubber works as well as other industries.

Another practice which has crept in, and not too long ago at that, is to use mixed stocks almost as soon as they leave the mixers. With some compounds this is of course possible, but it is not always universal, and where trouble is encountered once again the decision must be *no*. The principle of a 24 h maturing and relaxing period after mixing is in general as necessary at the present time as it was in 1936, when the author joined the industry, and it will also be necessary with many compounds in the future—so once again the stock must be chosen wisely when deciding to cut down maturing times.

It is necessary to make a laboratory check on all batches of mixed compounds for cure properties including hardness, for obvious reasons. Additionally, by careful selection of the compound, a frequency may be set for plasticity and specific gravity, together with rheometer testing as necessary. Once again it all depends on the compound and its use, plus experience gained with this compound over a period of time.

Another important point in designing a compound is its specific gravity. It is sometimes false economy to use too cheap a mix, as its volume cost will be higher than one containing more hydrocarbon. Also, this latter mix will more likely not only process better, but also faster, with a labour cost gain. It is therefore not only material costs that have to be closely examined, but also other closely allied factors.

Perhaps the greatest problem in all rubber factories is the sudden appearance of contamination, and this despite the fact that every care is taken with raw materials, mill room cleanliness and subsequent shop floor tidiness, and even after using strained and refined compounds. Good housekeeping is a must within a rubber works, and any sign of apparent relaxation of this must be immediately highlighted by process and quality control sections, together with the shop floor production management. This is their responsibility.

Malpractices of this nature that immediately come to mind are allowing the compounds to come in contact with the floor, plus operators walking all over the rubber. Allowing the trays of mixing units to become contaminated with tailings from previous batches, material trapped on Banbury conveyors and in the mill cheek plates, etc. All too often these points are allowed to go on unchecked.

A rather amusing story when told years later, although far from a joke at the time, was a problem of contamination experienced on a large scale. There was no set pattern, however, as grit, broken bricks and glass, cardboard, matches, even football coupons, were found in the rubber at various times, at irregular periods and in different compounds. The question of possible sabotage had also been considered and had not been totally ruled out, when to cut a long story and investigation short, an over zealous floor sweeper was seen immediately after lunch one day to be taking his morning's sweepings up the Banbury stairs. This was rather odd, so he was allowed to proceed, whereupon he opened the Banbury upper door and dropped his efforts into the Banbury! Upon being questioned he said that he had always done this, as he thought the Banbury was a large dust bin! He genuinely believed this, and it therefore goes without saying that even ridiculous occurrences can never be ruled out of an investigation such as this. *Observance* must always be one of the by-words for the process control personnel. Some chance, odd occurrence can often be the answer to some inexplicable problem.

Another serious instance of contamination experienced some years ago was that of chips of wood suddenly appearing in the compound. This became linked with the paraffin wax portion of the compound. In those days the paraffin wax was melted separately on the Banbury platform in large tanks and was measured in liquid form and added by hand to the mix, down the Banbury throat. Up to this time, the paraffin wax had been delivered in fine linen bags, but due to shortages, as well as other reasons, the deliveries came in wooden barrels, which had to be broken open. This was the source of the trouble. The simple solution to this was the fitting of a fine wire sieve in the melting tank, but the point being made is another one of *observance*, where a change of supply had been previously noted and remembered, and then the two instances linked together. There is no substitute for this type of experience and observance. It is essential to get on to the factory floor and *observe*, and even develop eyes in the back of one's head! Such hindsight can be helped and aided by gaining the confidence of the respective operatives concerned, who are normally only too pleased to co-operate, when they see that people are interested in their opinions also.

Just a couple of other points before leaving the mill room. Many slight irregularities in the compounds can be removed by batch blending, and also frequent cycling of the materials after maturing. Polychloroprene rubbers in particular should be watched carefully with regard to shelf life and storage.

Outside the mill room operations, calendering and extruding are perhaps the most widely used of the other important processing operations. Points to observe on the calender are correct bowl temperatures coupled with running speed. Once again misuse of the latter is perhaps the most frequent cause of bad work, and subsequent problems. Also the calender should be fed with small rolls of material from the warming mill, little and often, rather than with large rolls at less frequent intervals. The reason for this is one of temperature, as a large roll will be much cooler at its finishing end than when started with subsequent variations in sheet gauge and bad surface finish. Even holes may be produced in severe instances.

If the calender is being used as a means of preparing sheet for subsequent operations such as extrusion or as a grinding medium, adequate cooling of the stock is essential to prevent later scorch tendencies.

When considering the extrusion process, certain points are common, whether the extruder is of the hot feed type or one of the newer cold feed models. A lot has been said, and will continue to be said, as to the pros and cons of hot feed versus cold feed techniques, and the claimed economies of the latter but after very careful consideration of all the main points there is generally speaking very little between the two methods, although if long runs are possible, a hot feed mill system will give higher outputs, with greater consistency.

The feeding of an extruder in a constant and even manner is essential, and a roller feed on the extruder greatly assists this.

Whether this is direct drive or propelled by means of a slipping clutch mechanism depends as usual on personal choice coupled with local operating conditions and the processing properties of the particular compound. In general these points appear to be better served by feeding from a hot mill, as there is certainly less scorch tendency from a mill fed stock than when cold fed. This is particularly so when dealing with high Mooney compounds.

Furthermore, it is essential that the clearances of the screws are carefully watched, as when wear occurs the thrust of the compound is severely impaired with resultant fall off in output and again scorch tendencies. Screw wear is more rapid on cold feed machines.

Finally, it is very necessary to check regularly the waterways for efficient cooling in an extruder, and the cooling system of the scroll in particular as this can become blocked, more often than is generally realised.

It is usual to dust either the sheet after calendering (if a liner is not used) or the extrudate either by a dry or wet technique. In either case it is essential for obvious reasons that the dusting medium should be of a smooth texture and not 'gritty' in feel. This is a frequent source of grit contamination, if not carefully controlled. It is a fallacy to use cheap materials for this operation, and the temptation to do so, despite cost pressures, should be resisted strongly.

An instance of this occurred some years ago in an electric cable plant which, at that time, was bulk producing small household cable by the longitudinal process. Very severe rejections were occurring due to failures at the spark test operation immediately after vulcanisation. These failures had been examined and were obviously contaminated but the difficult question to answer was from where? The process control personnel concerned in the investigation quite correctly started in the mill room and worked through the process. The investigation found that the dusting talc in the chalk boxes on the insulating machines was gritty and this grit unfortunately had bedded into the soft and uncured rubber. Of course, during spark testing, failures occurred at these weak points. The simple operation therefore of changing the talc put the matter right. When such an investigation has been carried out it is then necessary to highlight the previous weak point in the system to ensure that this does not occur again. It is by this means that efficient processes are built up over a period of time.

Another rather controversial subject, but one that is nevertheless very pertinent, is that of piece work and similar schemes. It is accepted that some scheme is necessary to obtain satisfactory output, etc., production wise, but it is considered that some system incorporating measured day work would not only achieve this, but would also improve the waste and scrap problems, which should always be a high priority on the trouble shooting list.

Vulcanisation in general is, or should be, a comparatively trouble free operation, provided the compounds have been designed, mixed and processed correctly. The major factor to look for is that the steam is not wet whether the vulcanisation is pan or press cured. In this respect it is a fallacy to talk about curing at say 45 psi steam. The terminology should be 145 °C (293 °F) as temperature is the critical factor, not pressure. Just to be ridiculous, the pressure gauge could well read 45 psi with cold water. Indeed some years ago, this very set of circumstances literally happened when one of the boilers started priming badly and the temperature dropped many degrees, but the pressure gauge remained constant!

A useful and rapid control test for cure state, although strangely little used today, is the T/50 method. This is the temperature at which the elongation of a frozen specimen of cured rubber recovers to 50 % of its elongation after having been elongated to 100 %, frozen, and allowed to recover as the cooling bath warms up. This is a constant temperature for a particular compound, and is an extremely reliable check on cure state.

It goes without saying that process control, quality control and inspection departments must work very closely together and in harmony with the production departments, in the obvious joint interest of all. Statistical control is also an essential function which should be geared to monitor key and important areas in the manufacturing process and operation. It is for this reason that it is essential for reaching agreement on the correctness of a process with the production departments at the outset. The statistics fed back to them by the quality control department are then of value, and trends can be seen and corrected long before troubles arise.

Finally, it is essential in any investigation that the technical department personnel should listen to the shop floor operatives, as they are obviously closer to the problem. By doing so, mutual confidence is achieved. However, it is equally important that nothing should be taken for granted, or for that matter accepted at face value without further investigation, but this must of course be done as diplomatically as possible. Indeed, a process control man has also to be something of a psychologist and diplomat as well as a rubber technologist!

It is trusted that in what can but be a brief summary of the subject, some of the pitfalls mentioned and which are often encountered in the factory may be of use and interest to the newer members of the rubber industry and will be of assistance to them, in their future trouble shooting.

REFERENCE

1. Evans, C. W., *Powdered and Particulate Rubber Technology*, Applied Science Publishers, London, 1978.

CHAPTER 7

SAFE HANDLING OF RUBBER INGREDIENTS

Apart from the very obvious requirements of safety when processing rubber compounds on conventional equipment such as internal mixers, calenders, extruders, etc., and ensuring that these are all fitted (and regularly checked) with interlocks, safety bars, etc., and the operators are fully conversant with all safety procedures, there are also additional and very necessary safety requirements which are not quite so obvious. These include such items as fire hazards, fumes, dust, noise, materials used, etc. These are all of equal importance, and the law will ultimately require the necessary actions to be operative and taken. It is therefore, imperative that anyone connected with the working of a rubber factory is fully conversant with these requirements, whether the individual is attached to the production, engineering, technical or personnel staff.

The most important of the requirements are discussed in this chapter, but this is not, nor is it intended to be, an alternative to the reading and understanding of the relevant requirements as laid down by law.

RAW MATERIALS

The British Rubber Manufacturers Association handbook, dealing with and entitled '*Toxicity and Safe Handling of Rubber Chemicals*', is available and it is considered essential that this publication should be under continuous perusal. By very kind permission of the BRMA this extremely valuable code of practice has been extracted and is referred to in this chapter.

The code of practice has been prepared on the basis of information known as at 1st January 1978. There may be, throughout world industry as a whole, many factors outside the knowledge or control of the BRMA Health Advisory Committee and they cannot accept liability for any injury, death, sickness, loss or damage resulting from reliance upon the code of practice; *responsibility for complying with the relevant health and safety law remains with the rubber manufacturers at all times.*

The code of practice deals with the raw materials (rubbers and rubber chemicals) which are in general use in the rubber industry. Provided that they are handled in accordance with reasonable standards of industrial practice as referred, the vast majority of raw materials do not constitute any significant hazard. On the other hand it should be clearly understood that almost any chemical, can be hazardous if subjected to careless handling or abuse.

In the UK and several other countries suppliers of raw materials to the rubber industry are now required to provide information concerning any known hazard which may be associated with the use or handling of substances supplied, and users should always be well advised to take careful note of the information.

DEFINITIONS

Toxicity

The term toxicity, when used in the context of industrial processes, refers to the properties of chemical substances, and describes the adverse effects which may be experienced by humans as a result of skin contact, inhalation, or ingestion. Since all chemical substances, even sugar or common salt, may fairly be described as having a measurable toxicity, it should be understood that it is the relative toxicity and the ease of absorption which chiefly determine the effective toxicity of a chemical substance, and the extent and nature of any practical hazard which may result from its use. It follows that the evaluation of a toxic hazard in an industrial process must take into account the known toxic properties of the substance in use, the circumstances and conditions of industrial usage, and also the possibilities of human exposure and absorption. Clearly, those substances which readily penetrate the intact skin, which are volatile or which easily form respirable dusts, constitute a much greater potential toxic hazard than those which lack these characteristics. It is important also to distinguish between acute and chronic forms of toxicity. Acute toxic effects are those which follow immediately or shortly after a brief exposure to the chemical. They will mostly occur with substances which are highly volatile and irritant or which are potent systemic poisons. Chronic effects occur after a much longer period of repeated exposure to amounts of chemicals which are individually too small to give acute effects. Substances giving rise to chronic effects include cumulative poisons and carcinogenic chemicals.

Exposure to a toxic hazard most commonly arises from atmospheric contamination, and the principal mode of entry into the human body is by inhalation. Less commonly, a significant exposure hazard may result from ingestion or skin contact. Proper and careful control of the amount of toxic substances in the atmosphere is at all times essential in order to eliminate the risk of industrially induced toxic effects. The decision about what may constitute adequate environmental control will frequently depend upon the existence of accepted threshold limit values for particular chemical substances.

Threshold Limit Value

The TLV (threshold limit value) defines the atmospheric concentration of potentially harmful gases, vapours, and dusts, to which it is considered that the majority of workers may be repeatedly exposed day after day without adverse effects. Three categories of TLV are now quoted:

(*1*) *Threshold Limit Value–Time Weighted Average* (*TLV–TWA*). This is the time-weighted concentration for a normal 8 h workday or 40 h working week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.

(*2*) *Threshold Limit Value–Short-Term Exposure Limited* (*TLV–STEL*). The maximal concentration to which workers can be exposed for a period up to 15 min continuously without suffering from: (1) Intolerable irritation; (2) chronic or irreversible tissue change; or (3) narcosis of sufficient degree to increase accident proneness, impair 'self-rescue' or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 min between exposure periods, and provided that the daily TLV–TWA also is not exceeded.

(3) *Threshold Limit Value–Ceiling* (*TLV–C*). The concentration that should not be exceeded even momentarily.

The commonest form of TLV available at present is the TLV–TWA, and unless otherwise stated it is this value which is quoted. TLVs are based on the best available information from industrial experience, from human and animal studies, and when possible from a combination of all three. Full information on TLVs is published annually by the Health and Safety Executive (*Guidance Note EH 15*/[year], '*Threshold Limit Values for* [year]') and all concerned with industrial health should obtain and consult the current edition of this document. Most of the TLVs are derived from American sources, but there are a number of substances for which different values are used in the UK. Compliance with TLV standards is generally considered to be mandatory, although not statutory.

Lethal Dose (LD_{50})

When the toxicity of a substance is under investigation by animal experimentation it is customary, in order to determine its acute toxicity, to administer different oral dosage levels to discover at what level a single dosage will result in the death of 50% of animals tested. This dosage level is described as the LD_{50} (or lethal dose 50%) and it is expressed in terms of the weight of the substance administered per unit body weight of the particular species of experimental animal (i.e. mg/kg bodyweight). Using this measure the EEC has adopted the following classification for assessing toxicity.

EEC CLASSIFICATION

Oral LD_{50} — *Rating*
Less than 25 mg/kg—Highly toxic
25–200 mg/kg—Toxic
200–2000 mg/kg—Harmful

Substances with LD_{50} values in excess of 2000 mg/kg are unlikely to present any acute toxic hazard. This scale provides a useful guide which indicates how poisonous a substance may be if taken in a single dose on one occasion. It does not necessarily indicate the degree of practical hazard under industrial conditions of use, and it gives no indication of the possible effects of long-term exposure to lower dosage levels of the substance.

Carcinogenicity, Teratogenicity and Mutagenicity

Carcinogenicity is the capacity of some agent or chemical substance to induce cancer in man or other animal species. Teratogenicity is the capacity of an agent or chemical substance to induce abnormalities in the developing offspring during pregnancy (an important recent example of teratogenic effect resulted from use of the drug thalidomide). Mutagenicity is the capacity of some agent or chemical substance to induce genetic changes resulting from chromosomal alterations, changes which may be transmitted from parent to offspring.

These three specific effects of exposure to a chemical substance are not directly related to, and must be considered separately from, acute toxicity. Substances which are suspected of carcinogenic properties, and available evidence of carcinogenicity may, on occasions, be derived from tests for mutagenicity. It should be noted that only a very small proportion of industrial materials have ever been tested for carcinogenic, mutagenic or teratogenic activity, and even where such testing has been carried out by animal experimentation, the results cannot be presumed to apply with equal validity to man.

Skin Effects

Some substances used in rubber manufacture can adversely affect the skin. A product described as a *primary irritant* is one where contact is liable to result in a local inflammation brought about by direct action on the skin (e.g. the soreness or redness produced by household detergents) or by friction. An extreme example of primary irritant action could be actual burns produced by contact with acids and alkalis. Removal from contact by the adoption of appropriate measures usually effects a cure.

When a product is described as a *skin sensitiser*, the inflammation is caused by an allergic mechanism. In such a case the body becomes abnormally sensitive after exposure to the product and even slight further exposure may produce a severe skin reaction. This inflammation need not necessarily be restricted to the area of direct skin contact. Thereafter, avoidance of any further exposure whatsoever to the chemical (especially in the form of dust or fume) is usually necessary. Skin patch-testing may help to determine whether or not actual sensitisation has taken place, but the important observation of recurrence on exposure at work, and recovery after absence from the job, will usually confirm the diagnosis. A few rubber chemicals have both sensitising and primary irritant potential. The probability of skin sensitisation taking place under industrial conditions is difficult to predict for individuals.

Some rubber chemicals show no indication (either from clinical tests or industrial use) that they can act as either irritants or sensitisers. The probability that some of these chemicals will ever cause skin sensitisation potential are very likely to cause problems whenever good hygienic working practices are neglected, others may only rarely produce cases of skin sensitisation.

The possibility also exists of cross-sensitisation (sensitisation by one substance resulting in sensitisation to a different substance) which can lead to false positive results on subsequent skin patch testing. For this reason, while it is possible to say that certain substances are potentially active skin sensitisers or irritants, it is not possible to guarantee that a substance will never cause sensitisation in any individual in any circumstances.

Statements on skin sensitisation are, therefore, statements of probabilities as far as the majority of organic chemicals are concerned; and as with all rubber chemicals, good industrial hygiene and minimum contact with the skin should be the constant aim. Such practices will ensure that any risk of a harmful effect on the skin is reduced to an absolute minimum. Under good operating conditions experience has shown that less than 0·05% of persons working in a large tyre plant were affected to such a degree that a change of job was ultimately required.

The International Contact Dermatitis Research Group has listed some 20 rubber compounding ingredients as having some skin irritant or sensitising potential to a greater or lesser degree. Such listing should not imply that the chemical concerned is invariably irritant to human skin, only that clinical experience indicates that it might be.

INDUSTRIAL HYGIENE AND SAFE WORKING PRACTICES

Codes of Practice

Codes of practice are designed to secure the safety, health and welfare of people at work. The general codes outlined below define the recommended working procedures for handling compounding ingredients and other chemicals within the rubber industry. If these recommended procedures are carefully followed, a high standard of industrial hygiene will be ensured without introducing unacceptable restrictions into the manufacturing operations.

To be effective, recommended working procedures rely upon the understanding and personal care of the individuals who have to put them into practice. Everybody involved must, therefore, have adequate training, so that they have a proper understanding of the procedure, and its purpose. It cannot be overemphasised that careless handling or abuse of chemical substances can be hazardous, just as misuse of a normally safe machine can result in serious injury. The provisions of these codes should be made known to, and apply equally to, maintenance personnel, as well as to all management and operative staff.

The codes will define correct handling procedures and techniques; the requirements for the provision and use of protective clothing, washing facilities, and where appropriate, the need for additional local exhaust extraction to supplement general ventilation measures. The recommendations contained in these codes of practice imply a need for careful attention to such basic consideration as a sound layout and building structure, a good standard of engineering and plant design, and the constant maintenance of a high standard of general housekeeping. It is particularly important that the opportunity for achieving these objectives in a new plant should be taken at the design stage.

The success of the codes will depend not only upon a well presented and complete manual of instructions, but also on how clearly the procedures laid down and techniques required can be communicated to the workforce. Operatives should be given clear, firm and precise instructions on the various handling procedures to be observed. A pictorial display at the work post may sometimes be preferable to written or verbal instructions. The final pre-requisite for success is continuing responsible supervision which is vital if the full benefits of the codes are to be obtained.

Substantial advantages can be gained from a logical flow line of usage of chemicals. For example, where compounding ingredients in the initial stages are to be processed under the stricter conditions of Code B (see below) such chemicals might with advantage be grouped together both for convenience and ease of processing. Wherever possible, compounding ingredients should be used in a form which minimises dust formation during handling. Most rubber chemicals can now be obtained as pellets, granules, flakes or oil-coated powders, which reduce the amount of dust. Many of the more hazardous chemicals which require stringent handling precautions are available as convenient polymer masterbatches, or as prepacked dispersions. These should be used wherever possible.

Codes

Reference is made to two codes described as A and B. Code A sets out the basic requirements and minimum standards for handling any rubber chemical. Code B sets out standards for rubber chemicals which have greater toxicity, and therefore, require stricter control.

Recommendations for Limits of Atmospheric Contamination

Very few of the rubber chemicals used by the industry have been assigned official TLVs. Rubber factories almost invariably experience contamination of the working atmosphere by dusts from powders and fumes from hot rubber and solvent. The BRMA Technical Study Group has recently carried out an extensive survey of the environment in a number of UK rubber factories. The objective of this study has been to measure the level of dust and fume contamination in particular working areas, and relate it to a visual assessment of the atmosphere in those areas. Arising out of this study, the adoption of the following industry hygiene standards is recommended.

Dusts

Code A Materials

The published TLV for 'inert dusts' is 10 mg/m^3 total dust. It is at present appropriate for this level to be applied to Code A materials. Nevertheless, it is recognised that at this level some of these materials will give the appearance of an unacceptably dusty environment. It is therefore recommended that 10 mg/m^3 should be regarded as an absolute maximum, and that steps should be taken to reduce dust exposures to the minimum practical level below this.

Code B Materials

For most organic rubber chemicals, antidegradants, accelerators, etc.

there are no official TLVs in existence. For those materials, with an LD_{50} less than 2000 mg/kg, and classified as *harmful* by EEC regulations, it is recommended that the total dust level is maintained below $2{\cdot}5\,mg/m^3$. This is indicated in the relevant data sheets. For other raw materials, fillers, carbon black, etc., TLVs are recommended.

Hot Rubber Fumes

It is recommended that the level of atmospheric contamination by fumes from hot rubber should be measured as the cyclohexane-soluble fraction of material collected on a glass fibre filter. Using this parameter, atmospheric contamination should be maintained below $0{\cdot}25\,mg/m^3$. This limit can be applied only in areas not substantially contaminated by organic dusts.

Strict observation of these recommendations will afford the best practicable means of protection against acute or chronic toxic hazards, and any health risk inherent in the handling of rubber chemicals.

The above recommended standards are constantly under review in the light of experience.

Code A

Code A sets out the minimum standards required for handling any rubber chemical.

Personal Hygiene

Good personal hygiene at work is dependent on: The provision of appropriate facilities, including adequate washing, showering and changing rooms, clean and dirty storage lockers, and suitable arrangements for the consumption of food and drink away from work areas; an appreciation of the potential sources of industrial health hazard; the careful application of recommended procedures; a planned, clean and well organised working routine; and special attention to the siting of vending machines and/or drinking fountains.

Care must be taken to avoid the ingestion of small quantities of rubber chemicals, and food and drink should never be taken into, stored, or consumed, in areas where chemicals are handled. Smoking should also be forbidden in such areas, since apart from the possibility of creating a fire hazard, it may facilitate the ingestion or inhalation of toxic chemicals.

Handling

Since chemicals can only enter the body by being inhaled, swallowed or absorbed through the skin, they should always be handled in ways which minimise these types of exposure. Direct skin contact with chemicals should be avoided, and appropriate protective clothing should be worn when required. Care should be taken to transfer materials in ways which do not cause dust clouds or atmospheric vapour concentrations. Operative personnel must be provided with proper utensils (e.g. scoops, ladles, buckets and knives) which should be reserved for their prescribed purpose.

Storage and Disposal

Rubber chemicals should only be stored in well ventilated areas specially reserved for this purpose. They should be protected from excessive heat, cold or damp.

Careful note must be taken of any local regulations which may apply, such as those concerned with the storage of highly flammable liquids. Storage locations must take account of fire regulations. They must not impede the escape of occupants from any building, nor the access of fire fighting services. They should be planned in such a way as to minimise the risk of fire or combustion products spreading to other areas.

Drums, containers and other packages should be sound, purpose built and preferably supplied by the rubber chemical manufacturer. They should always be clearly labelled, with a description of the contents and a display of any appropriate hazard warning. Lids and caps of all containers should be tight, well fitting and should be replaced immediately after use.

Any spillages of powders or leaks from liquid containers should be cleaned up immediately in accordance with any recommendations supplied by the manufacturer of the product.

Subsequent disposal of spillage and waste must take full account of any local or national regulations (e.g. in the UK the Control of

Pollution Act 1974 and the Deposit of Poisonous Wastes Act 1972). Notification to the appropriate local authority may be required and disposal is normally arranged either by burial on an approved site or by burning under carefully controlled conditions. It should be noted that partly-used or empty packages containing residues of chemicals, may be subjected to similar regulations.

All rubber chemicals held in storage should be handled or transported only by properly trained and authorised personnel who are fully conversant with this code of practice and aware of any special instructions provided by the material supplier or laid down by transport regulations. It is sound practice to keep a detailed register of all materials stored, together with any recommendations relating to them and to have this register always readily available for consultation.

General and Local Exhaust Ventilation

Inhalation of chemical products in the form of mists, fine dusts, powder, or fumes should always be minimised by good general ventilation. At specific operating points there may additionally be a requirement for local exhaust ventilation to control the level of fume, vapour or airborne dust at the source of emission. It should be remembered that exposure to dust or fumes may be harmful to health, and exposure levels must at all times be kept at a minimum and should never exceed the appropriate TLV. In some circumstances, and as a temporary measure to avoid excessive exposure, breathing apparatus, or dust masks, may have to be provided and worn. Respirators should, however, never be regarded as a satisfactory long term solution other than for very brief exposures, and permanent measures to control dust and fumes at source should always be the primary objective.

Skin Protection and Protective Clothing

Prolonged or repeated contact with the skin should be avoided. Accidental splashes with liquids or contamination with excess dust should be washed off with plenty of soap and water or special skin-washing solutions, which may be provided in first aid boxes. The provision and use of protective clothing (e.g. gloves, aprons, hats, overalls, with long sleeves, etc.) appropriate to the conditions of handling should be standard practice.

Protective clothing or overalls should be kept in good repair and should be laundered and replaced at reasonable intervals. Clothing which is accidentally heavily contaminated should be replaced at once and the affected garments cleaned or disposed of safely. When liquids or oils are being handled, special protective clothing (such as impervious PVC coated gloves or aprons) is necessary. Adequate changing facilities and individual lockers (including separate lockers for clean and dirty clothes) should be provided.

A policy of good skin care should be implemented with appropriate instruction at the initial training stage. Suitable posters and advisory skin leaflets should be prominently displayed and issued as required to employees.

Adequate and convenient washing facilities should be provided for the use of operatives handling rubber chemicals. Washing should be encouraged before taking food at meal breaks, when using toilet facilities and at the end of the working shift.

The use of chemical or abrasive cleaners is not recommended for the skin of the hands or any other part of the body, as it frequently results in the development of skin irritation and dermatitis. It may, however, be appropriate to provide suitable barrier creams and proprietary cleansing gels, and to encourage operatives to use them.

Where solvents are used in production processes there is a risk of degreasing the skin, and the application of a suitable after-work cream is recommended. The use of such solvents for skin cleansing purposes should never be permitted. Any injuries involving the skin, however trivial, should receive prompt and efficient first aid and then subsequent treatment under medical supervision if required.

Eye Protection

It is a sensible precaution to ensure that the eyes are always protected from avoidable contamination by irritant or toxic substances. Nevertheless, those substances which appear in this code of practice and which have been grouped together in Code A, are not generally irritant, and do not normally require the use of specific eye protection. The use of eye protection is, however, always recommended when handling chemicals in liquid form.

First Aid and Medical Facilities

Simple first aid facilities should be kept readily and conveniently available, with trained qualified personnel in attendance. When there is a need for further skilled medical assistance, this should be sought immediately from the nurse, doctor or casualty department as local circumstances and provisions dictate.

Code B

Code B relates to the handling of chemicals which possess a known toxicity sufficient to create a hazard to health if inadequate precautions are taken. In addition therefore to the strict application of Code A, further measures will be required as indicated below.

Personal Hygiene

Those recommendations listed in Code A, apply equally to substances listed under Code B. It must however, be clearly understood that the consequences of any failure to implement Code A recommendations will be potentially much more serious with Code B materials. There should therefore, be thorough and regular cleaning of the work areas, preferably by vacuum methods, in keeping with a high standard of good industrial housekeeping. It is emphasised that these measures must be combined with strict observance of established procedures for safe and clean working.

Handling

Only the minimum quantity required of each Code B chemical should be kept in the workshop. Properly labelled containers should be provided, and these should be kept closed when not actually being used. Bags, cartons and drums should be clean on the outside, clearly labelled and protected from damage. There must be strict observance of filling levels for liquids. Direct skin contact with Code B chemicals must be prevented by the use of suitable protective clothing. Transfer of these chemicals must only be carried out at a location where dust or vapour which will be generated is removed by properly designed exhaust extraction.

Storage and Disposal

In general the recommendations for storage and disposal of Code A chemicals will also apply to those in Code B. Extra care should however be taken to prevent damage to containers of Code B chemicals during storage. It may, with advantage, be possible to group all Code B materials into a specified area of the stores, with appropriate protection and warning notices. All empty bags, cartons, drums or other packages no longer required, together with unused residues and waste collected from dust extraction systems, must be put into suitable containers to await disposal. This should be by incineration, burial or by other agreed controlled measures which comply with local or national regulations.

General and Local Exhaust Ventilation

Adequate and efficient local exhaust ventilation must be provided to control the emission of excess dust, fumes or vapours at points where they are emitted. The efficiency of the system should be checked regularly (not less than every six months). Where appropriate TLVs are laid down, these must be adhered to, and regular checks made to ensure that this is done.

Occupational hygiene facilities should be available in order to maintain a strict check on the working environment, and to ensure safe conditions. These may either be provided on site, or by some outside agency.

Approved respirators should be worn only when it is not possible to provide local exhaust ventilation, or when this is temporarily out of action. The provision of a clear reference guide for use of the correct approved respirator is recommended. Such individual respirators however, should only be used as a temporary expedient pending a return to adequate ventilation control of the dust or fume at source.

Skin Protection and Protective Clothing

The recommendations listed for Code A materials will apply also to Code B materials. With Code B materials, however, a very high standard of personal hygiene will be essential and washing facilities of a more comprehensive nature than those listed for Code A will be required. These will usually include the provision of showers, towels, soap, and barrier or cleansing creams. Operatives must be encouraged to make use of washing facilities before meal breaks and full showering facilities at the end of each shift. Adequate time for washing must be allowed to ensure that the facilities can be properly used under appropriate supervision. Where showers or bathing facilities are provided, it will be important to guard against the introduction and spread of fungus infection of the skin.

All protective clothing provided must be maintained in first class condition, and every encouragement should be given to operatives to ensure that full use is made of it. To this end, a programme of good skin care should be initiated during job training and subsequently continued, with an appropriate display of leaflets and/or posters.

Eye Protection

Information listed indicates those circumstances or conditions, in which eye protection is mandatory. The form of protection which is provided must always be appropriate to those circumstances and may take the form of safety glasses, eye shields or chemical goggles as necessary. Boxes containing special eyewash bottles should be provided and all personnel should be aware of their location and trained in their use. Supplies of fresh clean water should be readily available and in areas of special risk, e.g. where strong acids or alkalis are being handled, and emergency drench shower should be provided. The location of these facilities must be clearly indicated and unobstructed access maintained. Attention is drawn to the Protection of Eyes Regulations 1974.

First Aid and Medical Facilities

Medical, nursing and first aid personnel should be thoroughly familiar with the specific hazards and with the first aid treatments which may be required.

Special Category Materials

Some substances used in the rubber manufacturing industry are already subject to Government regulations, statutory instruments, codes of practice or other recommendations covering safe handling. In addition, the BRMA has in recent years published individual recommendations for certain other rubber chemicals, and it is important that users of these materials should be fully aware of such special requirements. In addition, the list of substances for which such regulations exist is given below, together with references where appropriate. It should be noted that this list has been drawn up to include substances which are relevant to the rubber industry, but that inclusion of a substance in this list does not mean it is used by the industry. In particular, many aromatic amines are, of course, not used by the industry.

Acrylonitrile monomer—*BRMA Bulletin No. 20*; US Department of Health, Education and Welfare, *NIOSH Current Intelligence Bulletin*—Acrylonitrile July 1st, 1977.
4-aminodiphenyl—Carcinogenic Substances Regulations 1967 (UK).
Antimony and its compounds.
Asbestos—*BRMA Bulletin No. 20.*
Benzene—US Department of Health, Education and Welfare, NIOSH Criteria Document 1974. Criteria updated and recommendations for a revised benzene standard issued August 1976.
Benzidine—Carcinogenic Substances Regulations 1967 (UK).
Cadmium and its compounds.
Carbon disulphide.
*Chlorinated solvents.
Chloroprene monomer—*BRMA Bulletin No. 20.*
Chromium and its compounds.
Di-anisidine.
Ethylene thiourea—*BRMA Bulletins 11 and 16.*
Induline/Nigrosine dyestuffs—*BRMA Bulletins 19 and 20.*
Isocyanates—Isocyanates in Industry—Operating and Medical Codes of Practice—*BRMA* 1977.
Lead and its compounds.
MOCA—*BRMA Bulletins 8 and 16.*
α and β-naphthylamine.
4-nitrodiphenyl.
Trichloroethylene.
T23P; tris BP; tris (2,3-dibromopropyl) phosphate—*BRMA Bulletins 18 and 20.*
o-toluidine.
Vinyl chloride monomer.

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* Exemption from the regulations is normally obtainable for methylene chloride and 1,1,1-trichloroethane.

Regulatory Hazard Warning Labelling

Under an EEC directive of 1967 and subsequent amendment, member countries must make the hazard warning labelling of certain specified substances a legal requirement. The UK Draft Regulations for Packaging and Labelling of Dangerous Substances, which implement the latest EEC directive, are about to become law and require anyone supplying the designated substances to label them with the chemical name, the general nature of risk and corresponding symbol together with the stipulated risk and safety phrases. Further information on this subject may be obtained by reference to the regulations.

Fire Precautions

The majority of rubber chemicals do not constitute any significant fire hazard at normal ambient or operating temperatures, and since the detailed consideration of fire prevention and fire fighting procedures is beyond the scope of this book, attention is drawn (in the data sheets which follow) only to those materials which are highly flammable or to those special circumstances in which a fire risk may involve also a risk of serious exposure to toxic fumes.

Where it is indicated merely that 'routine fire precautions are required', this assumes an awareness, on the part of the reader, that all industrial chemicals, if involved in a fire, should be regarded as a potential source of toxic fumes, against which appropriate precautions, such as the use of breathing apparatus should always be employed.

NATURAL AND SYNTHETIC RUBBERS

No special precautions are necessary in handling natural and synthetic rubbers in general. Certain specialised synthetic rubbers, e.g. polyurethane elastomers and some fluorocarbon rubbers, require careful handling, and in these cases users should follow the safety precautions provided by the material supplier.

Users are advised to check that the stabiliser incorporated in a synthetic rubber is one which is free from toxic hazard, e.g. where PBN is used its content of free β-naphthylamine should be less than 1 ppm.

Some synthetic rubbers, e.g. SBR 1712 contain highly aromatic oils, and precautions should be taken to exhaust any fumes arising when the rubbers are heated to normal processing temperatures.

Some concern has recently been expressed about possible toxic effects arising from residual monomers in polymers and copolymers containing butadiene, styrene, acrylonitrile, vinylidene chloride and chloroprene. As far as solid synthetic rubbers are concerned there is no evidence to suggest that any free monomers would be present at a level which could constitute a toxic hazard. Polychloroprene latices, but not polychloroprene rubbers, can release some chloroprene monomer, and when using these latices the working environment should be checked periodically for chloroprene contamination, using a detector tube. The TLV for chloroprene is currently 25 ppm.

Vinyl chloride monomer (VCM) may be present in small amounts in certain grades of PVC. Since it is now known that industrial exposure to VCM may cause the development in man of a rare form of cancer (angiosarcoma of the liver), there has been some concern about the possible danger to men employed on the fabrication of PVC. To date, however, the only established cases of industrial cancer have occurred amongst polymerisation workers, and there is no evidence of any hazard involving PVC fabricators who could not, in any event, be exposed to more than trace quantities of residual monomer present in PVC compound. The rubber industry is primarily concerned with PVC/nitrile blends in which the VCM content is also very low and the risk of significant exposure is almost certainly negligible. The BRMA has recommended users of PVC compound to ensure that atmospheric levels of VCM are not permitted to exceed 1 ppm.

REINFORCING AGENTS AND FILLERS

Carbon Blacks

Carbon blacks are now produced wholly from oil feed stocks and contain trace amounts of polynuclear hydrocarbons, some of which, when extracted and isolated, are known carcinogens.

However, carbon black adsorbs and binds these substances so that on evidence of extensive animal testing, they are not, under normal working conditions in the rubber industry, released in the body to cause physiological problems.

A TLV for carbon black of 3·5 mg/m^3 has been established. To achieve this level of operation a good standard of ventilation and extraction is necessary in all areas where carbon black is used or handled.[1]

Carbon black made from mineral oil (i.e. furnace black) is subject to certain special restraints when incorporated in rubbers destined for use in contact with foodstuffs.

The American FDA allows the finished rubber product to contain up to 50 % by weight of carbon black, but in rubber products intended for use in contact with milk or edible oils, furnace black must not exceed 10 % by weight of rubber product.

The Federal German Ministry of Health does not permit any carbon black under Recommendation XXI, covering general rubber goods used on contact with foodstuffs.

Some carbon black of defined purity is permitted in certain specified products which are covered by individual recommendations.

Mineral Fillers and Dusting Agents

The rubber industry uses a very wide range of mineral fillers as compounding ingredients and as dusting or lubricating agents. Care is necessary in handling these materials, as the dust arising from some of them can present a hazard to health. These include very dangerous and dangerous materials such as asbestos, use of which is subject to the asbestos regulations in many countries, and any materials containing more than 20 % of free crystalline silica, which are unlikely to be used in rubber manufacture. Others include moderate risk materials such as silicious minerals, e.g. mica, talc kieselguhr and graphite.

Threshold limit values for talc and mica are '1 mg/m^3 when present as very fine dust (e.g. cosmetic talc) otherwise 10 mg/m^3. Measurements should be based on total dust collected by a C.F. Casella cyclone sampler'.

Following a request by the BRMA for clarification of this statement, the UK Health and Safety Executive have stated that the limits to be applied to talc and mica are:

(i)	Total dust (respirable and non-respirable)	10 mg/m^3
(ii)	Respirable dust (i.e. that fraction of total atmospheric dust passing the Casella cyclone and being collected on the filter)	1 mg/m^3

It is necessary to satisfy both parts of this limit to produce an acceptable atmosphere.

The Health and Safety Executive have also pointed out that the limits now being introduced in the USA to control synthetic silicas are:

(i)	Total	5 mg/m^3
(ii)	Respirable ($< 5\ \mu$m)	2 mg/m^3

In the light of this information the following limits are recommended:

	Total dust	*Respirable dust*
Talc	5 mg/m^3	1 mg/m^3
Mica		
Fuller's Earth		
Graphite		
Kieselguhr (Diatomaceous Earth)		
Fumed silica (Aerosil, Cabosil)		
Precipitated silicas (Ultrasil VN3)		

It is important that the above substances should only be used with the appropriate general and local exhaust ventilation. The TLV should not be exceeded and Code B procedures should be adopted.

All other chemical fillers used in the rubber industry can be regarded as producing 'nuisance dusts' which are classified by HMFI under Group IV. *Guidance Note EH15/76* from the Health and Safety Executive, which adopts the American Conference of Governmental Industrial Hygienists (ACGIH) TLV's for chemical substances in workroom air, lists the standard for nuisance particulates as, 10 mg/m^3 of total dust $< 1\%$ quartz, or 5 mg/m^3 respirable dust. Code A procedures should be adopted for the substances below:

Calcium carbonate (whiting).
Clays, 1 % (max) free crystalline silica.*
Barytes, blanc fixe.
Lithopone.
Zinc oxide, zinc stearate.
Magnesium oxide.
Titanium oxide.
Aluminium hydroxide.
Precipitated calcium and aluminium silicates.
Glass fibre.

* UK produced rubber grade china clay has less than 1 % free crystalline silica.

TABLE 15

ANTIOXIDANTS/ANTIDEGRADANTS—HEALTH AND SAFETY FACTORS

Chemical name	*Abbreviation*	*Stains or discolours*	*Normal levels of use*	*Fire precautions*	*Health hazard*	*Acute oral LD_{50} (rat)*	*TLV recommended*	*Recommended handling code*	*Emergency first aid procedures*
Acetone-diphenylamine condensation product	ADPA	Yes	1–2	Non-flammable	Unlikely to be harmful by ingestion or skin absorption non-irritant to skin or eyes	>2 000 mg/kg	10 mg/m^3 total dust	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Quinoline polymerised 2,2,4-trimethyl-1,2-dihydroquinoline	TQ	Slight	0·5–3·0	Non-flammable	Unlikely to be harmful	>2 000 mg/kg	10 mg/m^3 total dust	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice.
Quinoline 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	ETMQ	Severe staining	1·0–3·0	Non-flammable	Slightly harmful by ingestion or skin absorption. Essentially non-irritant to skin and eyes	>2 000 mg/kg	—	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenyl-α-naphthylamine	PAN	Stains	1·0–3·0	Non-flammable	Unlikely to be harmful[a]	—	2·5 mg/m^3	B	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenyl-β-naphthylamine	PBN	Severe staining	0·5–2·0	Non-flammable	Unlikely to be harmful in a single dose[a]	>2 000 mg/kg	2·5 mg/m^3	B	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice.
Phenylenediamine *N,N'*-bis(1,4-dimethyl-pentyl)-*p*-phenylenediamine	77PD	Severe	1–2	Non-flammable	Harmful by ingestion. Skin unlikely by absorption. Eyes non-irritant	730 mg/kg	—	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice Vapour—remove contaminated clothng and fresh air.

Phenylenediamine	6PPD	Severe	1–2	Non-flammable	Ingestion/skin—unlikely Eyes—non-irritant	>2 000 mg/kg	10 mg/m^3 total dust	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenylenediamine *N*,*N*′-diphenyl-*p*-phenylenediamine	DPPD	Yes	1–2	Non-flammable	Ingestion/skin—unlikely Eyes—non-irritant	>2 000 mg/kg	10 mg/m^3 total dust	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenylenediamine *N*,*N*′-di-*β*-naphthyl-*p*-phenylenediamine	Anchor DNPD	Slight	0·2–1·0	Non-flammable	Ingestion/skin—unlikely[a]	>2 000 mg/kg	2·5 mg/m^3	B	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenylenediamine *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine	IPPD	Severe	1–2	Non-flammable	Skin—unlikely Ingestion—harmful Eyes—non-irritant	900 mg/kg	2·5 mg/m^3	B	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice Vapour—remove to fresh air
Phenylenediamine *N*,*N*′-bis(1-ethyl-3-methylpentyl)*p*-phenylenediamine	DOPD	Slight	1–2	Non-flammable	Skin—slight Eyes—non-irritant	>2 000 mg/kg	—	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Phenylenediamine (mixed)	Wingstay 100	Severe	1–2	Non-flammable	Respiratory—possible Skin/eyes—unlikely	>2 000 mg/kg	10 mg/m^3	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice Vapour—Remove to fresh air
Diphenylamine	ODPA	Yes	0·5–2·0	Non-flammable	Eye/skin—OK Ingestion—unlikely	>2 000 mg/kg	10 mg/m^3	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice
Hindered phenol	BHT BPH	No	1–2	Non-flammable	Eye/skin/ingestion unlikely	1700–1970 mg/kg	10 mg/m^3	A	Skin—wash liberally with soap and water Eye—irrigate with water and seek medical advice

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[a] Could contain *β* naphthylamine (a potent carcinogen) as impurity. Before using check the advice of the suppliers.

Pigments

Both organic and inorganic pigments are used by the rubber industry. The suppliers of these have provided information concerning the composition of the pigments they sell, and give advice regarding safe handling. Users of pigments should follow this advice.

Caution should be observed in use of antimony, cadmium and chromium pigments. Refer to relevant HSE guidance notes.

It should be borne in mind that many organic dyestuffs have been manufactured by processes which could result in free aromatic amines being present in the dye as sold. *Assurance should be sought from suppliers that the dyestuffs are controlled to an acceptable level of freedom from such amines and that no carcinogenic hazard exists.*

PROCESS OILS, WAXES, TACKIFIERS, ETC.; ESTER PLASTICISERS

Process Oils

It is customary to divide rubber process petroleum oils into three types—aromatic, naphthenic and paraffinic. These types can be simply characterised as follows:

Aromatic—60% aromatics (by Clay-Gel analysis), specific gravity 0·98–1·03, and flash point °C = ASTM D.92–72.
Naphthenic—30–60% aromatics (by Clay-Gel analysis), specific gravity 0·91–0·95, and flash point °C = ASTM D.92–72.
Paraffinic—30% aromatics (by Clay-Gel analysis), specific gravity 0·86–0·89, and flash point °C = ASTM D.92–72.

The aromatic portion of these mineral oils will contain some polycyclic aromatic hydrocarbons which have been associated with skin cancer in certain occupations where prolonged skin contact has occurred. The naphthenic and paraffinic oils are usually more highly refined and will contain less polycyclics than the aromatic oils. When handling these oils it is important that precaution details in Code B of the code of practice are followed.

It is common practice in modern rubber compounding to incorporate very high levels of mineral oils into certain mixes. With high temperature mixing, extruding, calendering and curing temperatures, at times exceeding 180 °C, excessive fumes may be evolved.

These must be controlled using suitable extraction equipment. It is advisable to use oils with the lowest volatile content possible.

Users of process oils can obtain further information regarding safety in handling of these from the following publications: (1) *Aromatic Petroleum Oils—Safety in Handling*. Issued by the Institute of Petroleum; (2) Dutrex Aromatic Process Oils, *Safety Data Information Sheet*, March 1978. Issued by Shell Chemicals, UK Limited; and (3) *Health Guide to BP Petroleum Products*. Issued by BP Oil Limited.

Petroleum Waxes

The rubber industry is mainly concerned with refined paraffin waxes and microcrystalline waxes, but some softer waxes containing free oil are also used. These do not present a hazard if Code A of the code of practice is followed. A TLV of $2\,mg/m^3$ is recommended for wax fumes, a level which is unlikely to be reached at rubber processing temperatures.

Tackifying and Reinforcing Resins

A very wide range of resins is used by the rubber industry. However, the majority will fall into one or other of the following classifications.

Petroleum Hydrocarbon Resins—Aliphatic

These pale coloured solid resins (e.g. Escorez 1000, Imprez 100) present no special toxic hazards providing Code A of the code of practice is followed.

Petroleum Hydrocarbon Resins—Aromatic

These materials (e.g. Picco 6000 series) may contain some polycyclic aromatic hydrocarbons, and should be handled according to Code B.

Coumarone Indene Resins

These resins consist mainly of polyindene, but are traditionally known as coumarone resins. They are normally obtained by coal tar distillation, and contain some polycyclic aromatic hydrocarbons. (Analysis of some UK produced grades of coumarone resins have shown the presence of 1–2 ppm benzo(*a*)pyrene.) They should be handled according to Code B.

Phenol Formaldehyde Resins (e.g. Cellobond Resin)

These are used by the rubber industry both as tackifying and reinforcing resins. They are usually polycondensates of phenols and aldehydes. At elevated temperatures they emit phenol vapour which may cause respiratory irritation and discomfort. Users should insist that the free phenol content is below 1 %. Prolonged skin contact may cause irritation. Handle according to Code B.

Ester Plasticisers

The rubber industry uses ester plasticisers mainly in nitrile rubbers and PVC/nitrile blends. These can be divided into the four main groups—phthalates, adipates, sebacates and phosphates. The following list covers those commonly used in rubber compounds.

Phthalate esters	*Abbreviation*	*TLV*
Dibutyl phthalate	DBP	5 mg/m^3
Di-isobutyl phthalate	DIBP	—
Di-2-ethyl hexyl phthalate	DOP	5 mg/m^3
Di-iso-octyl phthalate	DIOP	—
Di-alphanyl phthalate	DAP	—

Phthalate esters have a low oral and dermal toxicity and are non-irritant to skin and eyes. They may be safely handled using Code A.

Adipate and sebacate esters	*Abbreviation*
Di-2-ethyl hexyl adipate	DOA
Di-2-ethyl hexyl sebacate	DOS

These present no special toxic hazard during handling if Code A is followed.

Phosphate esters	*Abbreviation*
Tricresyl phosphate (or tritolyl phosphate—TTP)	TCP
Trixylyl phosphate	TXP

These substances are used widely in the rubber industry to improve flame resistance of rubber compounds. It is possible that commercial grades of TCP and TXP may contain impurities which are highly toxic. In the case of TCP it is well known that tri-*o*-cresyl phosphate can produce delayed neurotoxic effects in humans. Absorption can be through the respiratory tract or possibly through the skin. *O*-cresyl phosphates can be found in some commercial TXP. Certain suppliers offer grades of TCP and TXP free from *o*-cresyl phosphate and having much lower toxicity.

It is strongly recommended that TCP or TXP containing more than 0·1% of *o*-cresyl phosphate should not be used, *and users of these plasticisers should request full toxicity data from their suppliers.* Code B should be followed when handling TCP and TXP.

Use of Ester Plasticisers in Foodstuff Rubbers

	FDA Section 177.2600	*Federal German Ministry of Health*
DBP	Up to 30% by weight of product	Not approved
DIBP	Not approved	Not approved
DOP	Up to 30% by weight of product	Rec. XXI. Up to 10% by weight of product
DIOP	Not approved	Not approved
DOA	Up to 30% by weight of product	Rec. XXI. Up to 10% by weight of product
DOS	Up to 30% by weight of product	Not approved
TCP, TXP	Not approved	Not approved

MISCELLANEOUS

Organic Peroxides

Several of these materials are used within the industry as crosslinking agents for specific rubbers. Basically they are very active and unstable chemicals and should be handled with Code B procedures, including special precautions for storage.

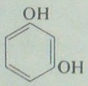
(1) Store in a cool (maximum temperature, 30 °C), dry place, away from sunlight and possible sources of ignition.
(2) Avoid contact with reducing agents which can cause decomposition.
(3) Always wear goggles and be careful not to spill.

The following are typical peroxides used in the rubber recipes, and in the main they can be obtained in dispersion form with inert fillers.[2,3]

Inert Fillers

Chemical name	*Trade name*	*Supplier*
Dicumyl peroxide	Dicup	Hercules
	Perkadox	Akzo
	Luperox	Harwick
1,1-di(tertbutyl peroxide) 3,3,5-trimethyl cyclohexane	Trigonox	Akzo
	Luperco	Harwick
Bis(tertbutyl peroxy isopropyl)benzene	Perkadox	Akzo
	Vul-Cup	Hercules
	Retilox	Montedison
4,4-ditertbutyl peroxy *N*-butyl valerate	Trigonox	Akzo
5-bis tertbutyl peroxy 2,5-dimethylhexane	Varox	Vanderbilt
	Luperco	Harwick
Tertbutyl peroxy benzoate	Trigonox	Akzo
Dibenzoyl peroxide	Lucidol	Akzo
Bis(2,4-dichlor benzoyl)peroxide	Perkadox	Akzo

Resorcinol

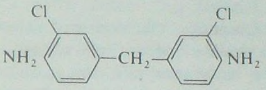
Chemical name	1,3-dihydroxy-benzene
Chemical formula	
Suppliers	Koppers (USA) L.B. Holliday
Melting point	Volatilises at 110 °C
Form	Small flakes
Specific gravity	1·27
Fire hazard	Non-flammable
Health hazard	Very harmful by ingestion Severe eye irritant Respiratory irritant Skin irritant
Acute oral LD_{50} (rat)	300 mg/kg
TLV	45 mg/m^3, 10 ppm
Handling code	B

Where fumes are present, as a result of processing conditions, such as at the dumping of an internal mixer, very adequate air extraction and circulation is necessary, and here it is advisable to keep environmental levels to less than 1 mg/m^3 wherever possible.

In its solid form it can be absorbed through the skin, causing itching and dermatitis.

Resorcinol is soluble in water, but insoluble in rubbers, and blooms to the surface of unvulcanised stocks. Skin contact, therefore, should be avoided.

Methylene Bis Ortho Chloroaniline (MBOCA)

Chemical formula	
Trade name	MOCA
Suppliers	Du Pont Hickson & Welsh
Melting point	103 °C
Specific gravity	1·44
Normal usage	As a crosslinking agent for polyurethanes
Fire precautions	Non-flammable, but if involved in a fire emits toxic fumes. Use water, foam or *carbon dioxide* extinguishers
Health hazard	Suspected bladder carcinogen
Acute oral LD_{50} (rat)	2100 mg/kg
Handling code	Special category material
Use in foodstuffs	Not approved

In the USA this material is considered to be a weak bladder carcinogen (from work carried out on dogs), and at present there is no evidence that MBOCA has caused cancer in man. However, the BRMA Health Advisory Committee recommends that this material should not be used, as the conditions which would have to be improved in order to ensure safe working, would be of such stringency as to render them impracticable and unacceptable.

Rubber Solvents

These may be divided into four categories:

(1) Low aromatic, i.e. $<20\%$ aromatic
(2) Aromatic
(3) Alcohols and ketones
(4) Chlorinated

Safety Precautions

Many of the precautions in the use and handling of solvents are of a common nature and may be grouped as follows.

Fire

With the exception of the chlorinated materials all rubber solvents are highly flammable, and it is very advisable to contact the local fire authorities as to their safe storage and use. In any case, many countries have their own regulations for these materials, which differ from place to place, and even from town to town, so outside advice is very necessary.

Obviously, all possible forms of ignition must be kept well clear of liquid and vapour sources.

Static electricity is a very real hazard and steps should be taken to ensure proper earthing of processing plant, etc. It is also very helpful to add small quantities of antistatic additives to the solvent in the main storage tanks. In this connection most of the main petroleum companies have proprietary branded materials and would give advice.

Health

All solvents have varying degrees of adverse effects on the human body, and should therefore be handled with respect. Fatigue is usually the first warning of trouble when handling solvents, and this is followed by headache, nausea, drowsiness, and loss of consciousness. Obviously therefore, plenty and adequate ventilation is essential.

Some solvents have rather pleasant odours, and it is necessary not to become 'hooked' by this, as the practice of 'solvent sniffing' is perhaps more widespread than realised. This is a gross misuse and is a highly dangerous and serious matter.

Recent evidence from animal experiments suggests that *benzene* in amounts greater than 1 % in solvents may constitute a long-term cancer hazard. It is, therefore, essential to control the use and type of industrial solvents.

Skin and Eyes

Eye irritation is produced with most solvents, including their vapours, and skin contact can produce defatting and dermatitis.

SPECIAL PRECAUTIONS

Aromatic Solvents

These are normally supplied with a maximum benzene concentration of 0·20 % wt/wt. Benz*e*ne has been associated with leukemia and should never be used as a rubber solvent. It is essential that the difference between benz*e*ne and benz*i*ne is fully understood. Benz*e*ne chemically is C_6H_6 and is highly toxic. Benz*i*ne is a widely used and misleading term, and in any case should be pronounced as in w*i*ne, but preferably the term should not be used at all.

Trichloroethylene

Like chloroform, this material has anaesthetic effects, and liver damage can be caused by over-exposure. If this material must be used, then strict air-control is necessary.[5]

Methylene Chloride

Until very recently, this material has been considered to be one of the safest chlorinated solvents. However, even this material requires plenty of fresh air in the vicinity as there is some evidence to show that the body converts, inhaled methylene chloride to carbon monoxide, resulting in elevated levels of carboxyhaemoglobin, with higher than normal levels of carbon monoxide in expired air.[6,7]

THRESHOLD LIMIT VALUES

The following figures are given as a guide only, and on *no account* should they be used as exact values in distinguishing safe and unsafe working conditions.[4]

Solvent	*Type*	*Specific gravity*	*Flash point (closed) (°C)*	*Boiling point (°C)*	*TLV ppm*
Low aromatic	SBP1	0·70	−46	35/115	125
	SBP2	0·71	−34·5	67/95	175
	SBP3	0·73	−9·5	98/122	275
	Rubber solvent	0·75	2	115/155	200
	White spirit	0·79	38	150/230	100
Aromatic	Solvent naphtha	0·84	7	95/143	100
	Toluene	0·87	4·5	110/112	100
	Xylene	0·86	23	137·5/144·5	100
Alcohols and ketones	MEK	0·81	−6	79/81	200
	Methyl ISO butyl ketone	0·80	13	114/117	100 (Skin)
	Methyl alcohol	0·80	12	64/66	200 (Skin)
	ISO propyl alcohol	0·82	16	79/81	400 (Skin)
Chlorinated	Perchlorethylene	1·62	None	118/122	100 (Skin)
	Trichlorethylene	1·46	None	86/87	200
	1,1,1-trichlorethane	1·32	None	70/80	350
	Methylene chloride	1·32	None	38/41	200

ENVIRONMENTAL MONITORING PROCEDURES

The following list of techniques are widely used, and are recommended as being necessary to ensure that the levels mentioned earlier in this chapter are adhered to. The experimental techniques themselves are not detailed as they are very adequately described in the BRMA handbook.

(1) Measurement of total dust concentrations.[8]
(2) Measurement of respirable dust.[9]
(3) Personal air sampling.
(4) Automatic sampling.
(5) Measurement of atmospheric solvent concentrations.
(6) Measurement of fumes from hot rubber.

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CHAPTER 8

CHEMICAL RESISTANCE

The type of polymer chosen for a particular rubber article's function depends upon consideration of temperature (both operating and ambient), the nature of the fluid or chemical in contact with the rubber and other relevant operating conditions. It also depends upon the actual percentage of the polymer in the compound, and in this connection the basic characteristics of most polymers can be varied by the introduction of copolymers (and blends), compounding ingredients, or reinforcing agents, to achieve the desired balance of properties.

Each grade of polymer is usually available in a range of hardnesses, this property being measured in IRHD (International Rubber Hardness Degrees). Ascending numbers indicate increasing hardness, the ultimate value being 100.

The table of chemical resistance (see Table 16) has been compiled to serve as a guide only, and should not be used as the ultimate authority. Exact operating conditions should be known before a final choice is made and rubber manufacturers should be consulted whenever possible, especially for the more corrosive materials.

It cannot be over-emphasised that the chemical resistances shown should be taken as a general guide only, since many of these characteristics are significantly affected by the environment of the operating conditions. Selection of the material for a particular and precise duty should be made in conjunction with the rubber manufacturer, and agreed before any final specification is issued. In this respect it is recommended that reference be made to BS 5176—British Standard specification for a classification system for vulcanised rubbers.

This standard has been prepared under the authority of the Rubber

Industry Standards Committee, as a reference classification for vulcanised rubbers. It provides a means of specifying the physical properties of vulcanised rubbers in a convenient notation. In the interests for rationalisation of test methods, it limits the times and temperatures available for selection in connection with certain tests.

The classification is based on the physical properties of the vulcanised rubber rather than on composition requirements and follows closely the system published by the American Society for Testing and Materials (ASTM designation, D2000) and also the ISO.

(Table 16 overleaf)

TABLE 16

CHEMICAL RESISTANCES (AT ROOM TEMPERATURE) OF POLYMERS

(1, Satisfactory; 2, should be satisfactory, but use with caution and seek advice; 3, unsatisfactory)

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Acetaldehyde	2	3	—	3	1	—	—	—	—	—	—
Acetamide	2	2	—	1	2	—	—	—	—	—	—
Acetic acid (dilute)	1	1	2	1	1	2	2	—	1	1	1
Acetic acid (glacial)	1	1	3	1	2	2	3	—	1	1	1
Acetic anhydride	1	1	2	1	1	1	3	—	—	1	1
Acetone	1	1	1	3	1	1	3	1	1	1	1
Acetophenone	2	3	—	3	1	—	—	—	—	—	—
Acetylene	1	1	1	1	1	1	—	1	1	—	1
Acrylonitrile	1	3	—	3	2	—	—	—	—	—	—
Air (70 °C)	2	2	1	2	1	1	1	1	1	1	1
Aluminium salts	1	1	1	1	1	1	1	—	—	1	1
Ammonia gas (cold)	1	1	1	1	1	1	—	2	—	1	1
Ammonia (liquid)	2	2	2	1	1	1	—	2	—	1	1
Ammonium carbonate	—	—	—	3	—	—	—	—	—	—	—
Ammonium chloride	1	1	1	1	1	1	1	2	1	1	1
Ammonium hydroxide	1	1	2	1	1	1	—	2	—	1	1
Ammonium salts	1	1	1	1	1	1	1	2	1	1	1
Amyl acetate	2	3	3	3	—	3	3	—	1	2	1
Amyl alcohol	1	1	1	1	1	1	1	—	1	1	1

Amyl borate	3	3	—	1	3	—	—	—	—	—	—
Amyl chloronaphthalene	3	3	—	2	3	—	—	—	—	—	—
Amyl naphthalene	3	3	—	3	3	—	—	—	—	—	—
Aniline	1	1	2	3	1	3	3	3	3	2	1
Aniline dyes	1	1	2	3	1	2	—	3	3	—	—
Aniline hydrochloride	1	—	—	3	—	—	—	—	—	—	—
Animal oil	3	—	—	1	1	—	—	—	—	—	—
Aqua regia	3	3	2	3	2	2	—	—	—	—	—
Arsenic acid	1	—	—	—	—	—	—	—	—	—	—
Asphalt	3	3	2	1	3	2	1	—	—	—	3
Barium hydroxide	1	1	1	1	1	1	1	1	—	1	1
Barium salts	1	1	1	1	1	1	1	1	1	1	1
Beer	1	1	1	2	1	1	1	1	1	1	1
Beet sugar liquors	1	1	1	1	1	1	—	1	—	—	1
Benzene	3	3	3	3	2	3	3	3	1	3	1
Benzaldehyde	3	3	2	3	1	2	—	3	—	—	—
Benzyl alcohol	1	2	2	3	1	2	—	3	—	—	—
Benzyl benzoate	2	3	2	3	1	2	—	3	—	—	—
Benzyl chloride	2	3	—	3	1	—	—	—	—	—	—
Borax	1	1	1	1	1	1	—	1	1	—	1
Boric acid	1	1	1	1	1	1	1	1	1	—	1
Bromine	3	3	3	3	3	2	—	—	3	2	2
Butane	3	3	1	1	3	1	1	1	1	1	1
Butyl acetate	3	3	3	3	2	3	3	—	2	2	—
Butyl acetyl ricinoleate	3	3	—	2	1	—	—	—	—	—	—
Butyl alcohol	1	1	1	1	1	1	1	—	—	2	1
Butyl stearate	3	3	—	1	3	—	—	—	—	—	—

(continued)

TABLE 16—*contd.*

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Calcium hydroxide	1	1	1	1	1	1	1	1	1	1	1
Calcium salts	1	1	1	1	1	1	1	1	1	1	1
Cane sugar liquors	1	1	1	1	1	1	1	1	—	1	1
Carbolic acid (phenol)	3	3	3	3	1	2	—	3	3	—	1
Carbon dioxide	1	1	1	1	1	1	1	1	1	1	1
Carbonic acid	1	1	1	1	1	1	1	1	1	1	1
Carbon bisulphide	3	3	3	2	3	3	—	—	2	2	2
Carbon monoxide	1	1	1	1	1	1	1	1	1	1	1
Carbon tetrachloride	3	3	3	3	3	3	2	1	3	2	1
Castor oil	1	1	1	1	1	1	1	1	2	1	1
Cellosolve acetate	2	2	3	3	1	—	—	—	—	—	1
Cellosolve butyl	1	1	—	1	1	—	—	—	—	—	—
Chlorine	3	3	3	—	2	3	3	3	3	3	2
Chlorinated solvents	3	3	3	3	3	3	—	1	3	—	1
Chloroacetic acid	—	2	2	2	—	1	—	—	—	—	1
Chlorobenzene	3	3	3	3	3	3	—	—	3	—	3
Chloroform	3	3	3	3	3	3	—	1	3	—	1
o-Chloronaphthalene	3	3	3	3	3	—	—	—	—	—	—
1-Chloro-1-nitroethane	3	3	3	3	3	—	—	—	—	—	—
Chlorosulphuric acid	3	3	3	2	3	3	—	—	3	—	2
Chromic acid	3	3	3	3	1	1	—	—	—	1	2

Citric acid	1	1	1	1	1	1	—	1	1	1	1
Copper salts	1	1	1	1	1	1	1	1	1	1	1
Corn oil	3	3	2	1	1	2	1	1	1	1	1
Cottonseed oil	3	3	2	1	1	2	1	1	1	1	1
Creosote	3	3	2	1	3	—	—	3	3	—	1
Cresols	3	3	3	3	3	—	—	3	3	—	1
Cyclohexane	3	3	—	1	3	—	—	—	1	—	—
Cyclohexanone	3	3	3	3	2	—	—	—	—	—	—
Dibenzylether	3	3	—	3	1	—	—	—	—	—	—
Dibutylphthalate	3	3	—	3	2	—	—	—	1	—	—
p-Dichlorobenzene	3	3	—	2	3	—	—	—	—	—	—
Diethylamine	1	1	—	1	1	—	—	—	—	—	—
Diethylene glycol	1	1	—	1	1	—	—	—	—	—	—
Diethylether	3	3	—	1	3	2	—	—	—	2	1
Diisopropylketone	3	3	—	3	2	—	—	—	—	—	—
Dimethylaniline	3	3	—	3	3	—	—	—	—	—	—
Dioxane	3	3	—	3	1	—	—	—	—	—	—
Dioxolane	3	3	—	3	2	—	—	—	—	—	—
Dipentene	3	3	—	2	3	—	—	—	—	—	—
Dioctylphthalate	3	3	—	2	2	—	—	—	1	—	—
Diphenyl	3	3	—	3	3	—	—	—	—	—	—
Diphenyloxides (Dowtherm®)	3	3	—	3	3	—	—	—	—	—	—
Ethanolamine	1	1	—	1	1	—	—	—	—	—	—
Ethers	3	3	3	3	3	2	—	1	—	2	1
Ethyl acetate	3	3	3	3	1	3	3	—	2	2	1
Ethyl alcohol	1	1	1	1	1	1	1	—	1	1	1
Ethyl acetoacetate	1	1	—	3	1	—	—	—	—	—	—

(continued)

TABLE 16—*contd.*

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Ethyl benzene	3	3	—	3	3	—	—	—	—	—	—
Ethyl cellulose	1	1	2	1	2	—	2	—	—	2	2
Ethyl chloride	1	1	2	1	1	2	2	—	—	2	2
Ethylene chlorohydrin	2	2	—	3	1	—	—	—	—	—	—
Ethylene dichloride	3	3	—	2	3	—	—	—	3	—	—
Ethylene glycol	1	1	1	1	1	1	1	—	—	1	1
Ethyl mercaptan	3	3	3	3	3	3	3	—	—	3	3
Ethyl oxalate	1	1	—	3	1	—	—	—	—	—	—
Ethyl pentachlorobenzene	3	3	3	2	3	—	—	—	—	—	—
Ethyl silicate	2	2	—	1	1	—	—	—	—	—	—
Fatty acids	3	3	2	2	1	1	1	—	1	1	1
Ferric chloride	1	1	1	1	1	1	1	—	1	1	1
Ferric sulphate	1	1	1	1	1	1	1	—	1	1	1
Fluorobenzene	3	3	3	3	3	—	—	—	—	—	—
Formaldehyde	1	1	2	1	1	1	1	1	2	1	1
Formic acid	1	1	2	1	1	1	1	—	2	1	1
Freon 12®	3	3	1	1	3	—	1	1	2	—	2
Freon 21®	3	3	3	3	3	—	—	2	2	—	—
Fuel oil	3	3	2	1	3	1	1	1	1	1	1
Furfural	3	3	2	3	1	1	3	—	—	1	1

Gasoline	3	3	3	1	3	3	1	1	1	3	1
Gelatin	1	1	1	1	1	1	1	—	1	—	1
Glucose	1	1	1	1	1	1	1	1	—	—	1
Glue	1	1	1	1	1	1	1	—	1	—	1
Glycerol	1	1	1	1	1	1	1	—	1	1	1
Hydraulic fluids											
petroleum based	3	3	1	1	3	1	1	1	1	1	—
phosphate ester alkyl	3	3	3	3	1	3	3	1	1	1	—
phosphate ester aryl	3	3	3	3	1	3	3	1	1	2	—
phosphate ester blends	3	3	3	3	1	3	3	1	1	2	—
silicate ester	3	3	3	3	1	2	2	1	1	2	—
water glycol	1	1	1	1	1	1	1	1	1	1	—
Hydrobromic acid	1	2	2	2	1	1	—	—	—	1	2
Hydrochloric acid (conc.)	1	1	2	1	1	2	3	—	3	1	1
Hydrocyanic acid	2	2	2	2	—	1	—	—	—	—	—
Hydrofluoric acid	2	2	3	2	1	1	—	—	3	1	1
Hydrofluosilicic acid	1	2	2	2	1	—	—	—	—	1	2
Hydrogen	1	1	1	1	1	—	1	1	1	—	1
Hydrogen peroxide	2	2	2	1	1	2	—	—	—	1	—
Hydrogen sulphide	1	1	1	1	1	1	—	—	1	—	1
Hypochlorous acid	1	—	—	—	—	—	—	—	—	—	—
Hydroquinone	1	—	—	—	—	—	—	—	—	—	—
Isobutyl alcohol	1	2	—	2	1	—	—	—	—	—	—
Isopropyl acetate	2	3	—	3	1	—	—	—	—	—	—
Isopropyl alcohol	1	2	—	2	1	—	—	—	1	—	—
Isopropyl chloride	3	3	—	2	3	—	—	—	—	—	—
Isopropyl ether	3	3	—	1	3	—	—	—	—	—	—
Kerosine	3	3	2	1	3	2	1	1	1	1	1

(continued)

TABLE 16—*contd.*

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Lacquers	3	3	3	3	3	3	3	1	2	—	2
Lacquer solvents	3	3	3	3	3	3	3	1	2	—	2
Lactic acid	1	1	1	1	1	1	—	—	1	—	1
Lead salts	1	—	—	—	—	—	—	—	—	—	—
Linseed oil	3	3	2	1	1	1	1	1	1	1	1
Lubricating oils	3	3	2	1	3	2	1	1	1	1	1
Magnesium salts	1	1	1	1	1	1	1	2	1	1	1
Maleic acid	1	—	—	—	—	—	—	—	—	—	—
Maleic anhydride	1	—	—	—	—	—	—	—	—	—	—
Malic acid	1	—	—	—	—	—	—	—	—	—	—
Mercuric chloride	1	1	1	1	1	—	—	3	1	—	—
Mercury	1	1	1	1	1	1	1	1	1	—	1
Mesityl oxide	3	3	—	3	2	—	—	—	—	—	—
Methyl alcohol	1	1	1	1	1	1	1	—	1	1	1
Methyl chloride	3	3	3	3	1	3	—	—	3	—	1
Methyl ethyl ketone	3	3	3	3	2	2	3	—	2	2	1
Methyl formate	2	2	—	3	2	—	—	—	—	—	—
Methyl isobutyl ketone	3	3	3	3	2	2	3	—	—	1	1
Methyl isopropyl ketone	—	—	3	3	—	2	3	—	—	1	1
Methyl methacrylate	3	3	3	3	2	—	—	—	—	—	—
Methyl salicylate	—	—	—	3	—	—	—	—	—	—	—

Milk	2	2	2	1	1	1	1	1	—	1	1
Mineral oils	3	3	2	1	2	1	1	1	1	1	1
Monobromobenzene	3	3	—	3	3	—	—	—	—	—	—
Monochlorobenzene	3	3	—	3	3	—	—	—	—	—	—
Monomethylether	2	2	—	1	1	—	—	—	—	—	—
Naphtha	3	3	2	1	3	2	1	1	1	2	1
Naphthalene	3	3	3	3	3	—	—	—	2	—	—
Naphthenic acid	—	—	—	1	—	—	—	—	—	—	—
Natural gas	2	2	1	1	3	1	1	1	1	1	1
Nickel salts	1	1	1	1	1	1	1	—	—	1	1
Nitric acid (dil.)	2	2	2	2	1	1	3	3	2	1	2
Nitric acid (conc.)	3	3	3	3	2	2	3	3	3	3	2
Nitrobenzene	3	3	3	3	1	3	3	—	3	2	1
Nitroethane	1	2	3	3	1	—	—	—	—	—	—
Nitromethane	1	1	3	3	1	—	—	—	—	—	—
1-Nitropropane	2	2	3	3	1	—	—	—	—	—	—
Oleic acid	2	2	2	2	1	1	—	1	1	1	1
Oleum spirits	3	3	2	—	—	—	—	3	3	—	2
Oxalic acid	2	2	2	2	1	1	1	1	—	1	1
Oxygen	2	2	1	2	1	—	1	1	1	1	1
Ozone	3	3	2	3	1	—	—	3	3	—	—
Palmitic acid	2	2	1	1	1	1	1	—	1	1	1
Perchloroethylene	3	3	3	3	3	3	1	—	3	2	1
Petroleum oils	3	3	1	1	3	2	1	1	1	2	1
Phenylbenzene	3	3	3	3	3	—	—	—	—	—	—
Phenyl ethyl ether	3	3	3	3	3	—	—	—	—	—	—
Phenylhydrazine	1	2	—	3	2	—	—	—	—	—	—
Phorone	3	3	—	3	1	—	—	—	—	—	—

(continued)

TABLE 16—*contd.*

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Phenol	3	3	3	3	1	2	—	3	3	1	1
Phosphoric acid	1	2	2	1	1	1	—	—	—	1	1
Picric acid	—	—	2	2	—	1	—	—	—	—	2
Pinene	3	3	—	2	3	—	—	—	—	—	—
Pine oil	3	3	2	2	3	—	—	—	—	—	—
Piperidene	3	3	—	3	3	—	—	—	—	—	—
Plating solutions:											
chrome	3	—	—	—	—	—	—	—	3	—	—
others	1	1	1	1	1	—	—	—	—	—	1
Potassium cyanide	1	1	1	1	1	1	1	—	—	1	1
Potassium hydroxide	1	1	1	1	1	1	1	—	1	1	1
Potassium salts	1	1	1	1	1	1	1	2	2	1	1
Producer gas	3	3	1	1	—	1	1	1	1	1	1
Propane	3	3	1	1	3	1	1	1	—	1	1
Propyl alcohol	1	1	1	1	1	—	—	—	—	—	—
Pyridine	3	3	3	3	1	—	—	—	3	—	—
Pyroligneous acid	1	2	3	3	1	—	—	—	—	—	1
Pyrrole	2	2	—	3	3	—	—	—	—	—	—
Salicylic acid	1	—	—	—	—	—	—	—	—	—	—
Sewage	1	1	1	1	1	1	1	1	1	1	1
Silver nitrate	1	—	—	—	—	—	—	—	—	—	—

Sodium hydroxide (dil.)	1	1	1	1	1	2	1	—	1	1	1
Sodium peroxide	3	3	3	3	1	1	—	—	—	—	1
Sodium salts	1	1	1	1	1	1	1	1	1	1	1
Soybean oil	3	3	2	1	1	1	1	1	1	1	1
Stannous chloride	1	1	1	1	1	1	1	—	1	1	1
Stannic chloride	1	1	1	1	1	1	1	—	—	1	1
Steam (200 °C)	3	3	3	3	1	2	3	3	3	—	3
Stearic acid	2	2	2	2	1	2	1	—	1	—	1
Stoddards solvent	3	3	3	2	3	—	—	—	—	—	—
Styrene	3	3	3	3	3	—	—	—	—	—	—
Sucrose solutions	1	1	1	1	1	1	1	1	—	1	1
Sulphur	2	2	1	1	1	1	1	—	1	1	2
Sulphur chloride	3	3	2	2	3	1	—	—	—	—	1
Sulphur dioxide	2	2	2	3	1	1	1	—	1	—	1
Sulphur trioxide	2	2	2	3	1	1	—	—	—	—	1
Sulphuric acid (dil.)	1	1	1	2	1	1	1	3	1	1	1
Sulphuric acid (conc.)	3	3	3	3	2	1	3	3	3	3	1
Sulphuric acid (fuming)	3	3	3	3	3	3	3	3	3	3	3
Sulphurous acid	1	1	1	1	1	1	2	3	2	1	1
Tannic acid	1	2	1	1	1	1	1	—	1	1	1
Tartaric acid	1	1	1	1	1	1	1	—	1	1	1
Tar	2	2	2	1	3	2	1	—	—	—	3
Terpineol	3	3	—	1	2	—	—	—	—	—	—
p-t-Butyl catechol	2	2	3	3	1	—	—	—	—	—	—
t-Butyl mercaptan	3	3	3	3	3	—	—	—	—	—	—
Tetralin	3	3	3	2	3	—	—	—	—	—	—
Toluene	3	3	3	3	3	3	3	1	2	3	1
Triacetin	1	1	1	1	1	—	—	—	—	—	—

(continued)

TABLE 16—*contd.*

Chemical	*Natural poly-isoprene*	*SBR*	*Neoprene CR*	*Nitrile NBR*	*Butyl EPDM EPT Chloro-butyl*	*Hypalon CSM*	*Hydrin CO ECO*	*Nylon*	*Hytrel PFTP*	*CM*	*XPLE*
Tributyl phosphate	2	2	3	3	2	—	—	—	—	—	—
Tributyl ethyl phosphate	2	2	3	3	2	—	—	—	—	—	—
Tricresyl phosphate	1	1	3	3	1	—	—	—	—	—	—
Triethanolamine	1	1	1	1	1	—	—	—	3	—	—
Trichloroethylene	3	3	3	3	3	3	3	1	3	3	1
Turpentine	3	3	2	1	3	3	1	1	—	1	1
Vegetable oils	2	2	1	1	1	1	1	—	1	1	1
Vinegar	1	1	2	1	1	1	—	1	1	1	1
Water	1	1	1	1	1	1	1	1	1	1	1
Whisky	1	1	1	1	1	1	1	1	—	1	1
Wines	1	1	1	1	1	1	1	1	—	1	1
Xylene	3	3	3	3	3	3	3	1	2	3	1
Zinc salts	1	1	1	1	1	1	1	—	1	1	1

CHAPTER 9

GLOSSARY OF RUBBER INDUSTRY TERMS

ACS: the abbreviation for the American Chemical Society.
ANSI: the abbreviation for the American National Standards Institute.
antioxidant: a compounding ingredient used to retard deterioration caused by oxygen.
antiozonant: a compounding ingredient used to retard deterioration caused by ozone.
ASTM: the abbreviation for American Society for Testing and Materials.
autoclave: a pressure vessel used for vulcanising rubber products by means of steam under pressure.
autoclave press: steam pan incorporating means for applying mechanical pressure to mould(s).

bale cutter: press in which a bale of raw rubber is forced against a knife, so cutting it into pieces for more convenient handling.
ball mill: rotating drum, generally mounted horizontally and containing loose balls of hard material to pulverise coarse particles.
Banbury mixer: a specific type of internal mixer.
bank: accumulation of material at the opening between the rolls of a mill or calender or at a spreader bar or knife.
batch: product of one mixing operation in an intermittent process.
bin curing: unintentional vulcanisation of a mix during storage.
blank (slug): piece of mix of suitable volume for the mould.
blender: vessel, fitted with movable blades, to convert the contents, usually compounding ingredients, into a uniform, homogeneous mixture.
blister: a raised spot on the surface or a separation between layers usually forming a void or airfilled space in the vulcanised article.

blister bar: bar parallel to a calender roll intended to minimise blistering during multiple bank calendering.

bloom: a discoloration or change in appearance of the surface of a rubber product caused by the migration of a liquid or solid to the surface, e.g. sulphur bloom, wax bloom. Not to be confused with dust on the surface from external sources.

bowl: term sometimes used for a calender roll.

box: roller on which long lengths of rubber sheets or fabric are wound and temporarily stored during the processes of manufacture.

breakdown: preliminary softening by mechanical work of raw rubber or a mix to render it more suitable for masticating, mixing or further processing.

breast roll: roll whose axis is arranged parallel to that of the other rolls but not in the same vertical plane.

bridge: two-spoked member supporting the core in the head of the extruder.

BRMA: the abbreviation for the British Rubber Manufacturers Association.

BSI: the abbreviation for the British Standards Institution.

bump (*breathe*)*:* momentarily to open and close a mould at an early stage in the moulding process to expel gas.

calender: machine with two or more rolls for converting rubber, or a combination of rubber with other materials, into sheet of a controlled thickness.

camber: convexity of the longitudinal section of a roll.

cement: a dispersion of unvulcanised raw or compounded rubber in a suitable solvent, used as an adhesive or sealant.

centre (*cone*)*:* that part on the die which shapes the internal profile of an extrudate.

chalk blower: device for applying a powder to the inner surface of a tubular extrudate as it leaves the die.

chatter marks: defect on calendered sheeting consisting of transverse narrow bands of alternately thicker and thinner material.

cloth mark: impression left on rubber by a fabric.

cold checks: defect on calendered sheeting consisting of surface roughness.

cold cure: vulcanisation at room temperature, commonly by means of sulphur monochloride solution or vapour.

composition: kinds and proportions of all ingredients contained in a mix.

compound (*mix*)*:* intimate mixture of a polymer(s) with all the ingredients necessary for the finished article.

compression mould: mould for compression moulding.
compression moulding: moulding process in which the blank is placed directly in the mould cavity and compressed to shape by closure of the mould.
continuous cure/vulcanisation (*cv*): vulcanisation by the continuous passage of extruded, calendered or spread material over or through a unit which is capable of rapid and complete heat transfer, e.g. liquid or salt bath, fluid bed, microwave, rotary cure, hot air cure, steam cure.
core pin: pin, being part of a mould, to form a hole in a moulding.
cracker: heavy-duty mill having two deeply-corrugated or pyramid-cut rolls to break down rubber, a mix, or for cutting rubber or a mix to pieces.
creel: apparatus for holding a large number of bobbins or spools of textile or steel cord allowing the cords to be brought together to form a layer.
cross/skew axis: adjustment to the contour of the nip form between two rolls of a calender by skewing the axis of one roll relative to the other.
crowsfeet: small flowmarks of V shape on calendered sheeting.
cure: vulcanisation; process of smoking coagulum.

daylight: distance between adjacent platens of a daylight press in the open position.
daylight press: press having two superimposed platens, usually heated, between which moulds are pressed.
die: detachable part of an extruder to produce the profile of an extrudate.
die holder: device for locating the die in relation to the extruder head.
die line: longitudinal raised identification line formed deliberately on an extrudate.
dipping: process for manufacturing seamless articles by dipping a former into a rubber solution or latex.
doubling machine: machine with two rolls for building thicker sheeting from plies of thinner sheeting.
dough: paste-like mass of smooth texture consisting of a mix and solvent for spreading.
dough mill: mill for homogenising dough.
draw: taper on the member(s) of a mould to facilitate the extraction of a moulding.
durometer: an instrument for increasing the hardness of rubber.
dusting or chalking (*the act of*): application of a powder to a rubber surface to prevent adhesion to another surface.

edge wheel: hand tool comprising a wheel with a narrow smooth edge for consolidating a join.

embossing machine: machine with two or more rolls for embossing sheeting.

extrudate: product of extrusion.

extruder (*tuber*): machine for extrusion, generally with a driven screw, for continuous forming of rubber or plastic through a die.

extruder head: that part of an extruder which houses the die or die holder.

extrusion mark or score line: mark or line formed accidentally in an extruder on an extrudate.

face cloth: fabric treated to give a smooth finish and used for temporary support of sheet rubber.

fish back (*Herringbone bar*): bar with corrugations so arranged that, when taut fabric is drawn across it, longitudinal wrinkles are removed.

flat cure: vulcanisation during which the value of a desired property proceeds to a maximum and then remains nominally constant for a substantial period after the initial change.

floating platen: platen suspended between the top and bottom platens of a multi-daylight press and capable of vertical movement.

flow marks: marks or lines on mouldings, caused by imperfect fusion of flowing fronts.

former: shaped rigid object on or in which a rubber article is formed either by dipping, moulding or manipulation and from which it is subsequently removed.

formulation (*recipe*): statement of all ingredients and their proportions to be contained in a mix.

frame: metal plate with a large, shaped hole which, when used between flat plates, forms a mould.

friction ratio: ratio of surface speeds of two adjacent rolls (mill or calender).

frictioning: process of impregnating woven fabric with rubber using a calender whose rolls rotate at different surface speeds.

grain: the misdirectional orientation of rubber or filler particles resulting in anisotropy of rubber compounds.

granules: particles larger than 1 mm.

gum dipping: process of impregnating textile with rubber by immersion in rubber solution.

heat resistance: the property or ability to resist the deteriorating effects of elevated temperatures.

heat stretching/stabilising: process of adjusting the thermal and dimensional properties of a fabric under specific combinations of temperature, tension and time.

hot air cure: process of conducting vulcanisation in heated air.

hot water cure: process of conducting vulcanisation in hot water or aqueous solution.

injection moulding: moulding process in which mix is forced into a closed heated mould from a separate heating chamber.

insert: component made of metal or other material, which is to become an integral part of a rubber moulding.

insert pin or moulding pin: pin to place and hold in position an insert during a moulding operation.

intermix: a specific type of internal mixer.

internal mixer: mixer having specially shaped rotor or rotors operated in a closed chamber.

IRI: the abbreviation for the Institution of the Rubber Industry (now PRI).

ISO: the abbreviation for International Organisation for Standardisation.

knife bar: bar carrying knives arranged for cutting sheeting longitudinally.

land: contact area substantially normal to the direction of closing between two separate parts of a mould.

lead press cure: a process wherein a lead sheath acts as a restraining member or mould, during vulcanisation.

lease bars: two or more metal bars interposed laterally between adjacent cords of a layer of cords to facilitate identification and tracing of individual cords.

let-off gear: apparatus for releasing material from a reel or box under controlled tension.

light resistance: the ability to retard the deleterious action of light.

linear: sheet material used for temporarily interleaving sheets which would otherwise stick together.

low temperature cure: vulcanisation at a lower temperature than usual for a particular product.

LPG: liquefied petroleum gas.

masterbatch (*MB*): homogeneous mixture of rubber and one or more compounding ingredients for use as a new material in the preparation of the final mix.

mastication: process of plasticising raw rubber irreversibly by the combined action of mechanical work and oxygen frequently at elevated temperature.

migration: a form of diffusion of compounding ingredients in a mix.

mill: machine with two driven rolls forming a nip for masticating, plasticising, mixing or sheeting.

mill bush (*breaker pad*): member fitted into the frame of a mill or calender, designed to break preferentially in the event of overloading.

mixer: machine used for mixing together polymers and compounding ingredients.

Mooney viscometer: rotation instrument used as a measure of the effective viscosity of the rubber. The answer obtained is known as the Mooney value.

mother stock: type of masterbatch in which the ingredients are present in a higher proportion than required in the final mix. NB. Masterbatches are used to facilitate processing or enhance the properties of the final product, or both.

mould finish: surface finish of mould.

mould lubricant: material applied to a mould to prevent adhesion of the rubber to the mould.

mould mark: surface imperfection transferred to a moulding from corresponding marks on a mould.

mould register: means of correctly aligning the parts of a mould.

moulded finish: surface finish of a moulding as it leaves the mould, no subsequent operations having been performed.

moulded skin: surface layer of a moulding which may differ slightly from the bulk of the material in the moulding.

moulding pressure: force applied by the press divided by the projected area of the mould cavity(ies).

moulding process: process of shaping a material with a die or mould by applying pressure and usually heat.

moulding product: object produced in a closed mould (e.g. by compression moulding, injection moulding or transfer moulding).

moulding shrinkage: difference in dimensions between a moulding product and the mould cavity in which it was moulded, both the mould and the moulding product being at normal room temperature when measured.

MRPRA: the abbreviation for the Malaysian Rubber Producers Research Association.

multi-daylight press: daylight press with more than one opening.

nerve: state of insufficient mastication.

nip: line of surface contact between two rolls, or the gap between them in the plane of their axes.

offset moulding: product of a mould whose parts are not in register.

open-sided or swan-neck press: cantilever press with columns on one side only and whose opening is therefore accessible for loading from three sides.

open steam cure: vulcanisation without a mould, in steam.

optimum cure: condition of vulcanisation to achieve an acceptable compromise between a number of desired properties or the optimum value of a selected property.

overcure: a state of cure greater than the optimum.

ozone cracking: the surface cracks, checks, or crazing caused by exposure to an atmosphere containing ozone.

peak cure: vulcanisation during which the value of a major property proceeds to a maximum or minimum and then changes rapidly.

pelletiser: machine similar to a strainer for preparing pellets of rubber.

platen: flat metal plate or chest to apply heat and pressure to mould(s) in a press.

plucking: tearing out of isolated portions from a rubber surface during separation from a second surface.

post cure: secondary cure, at a controlled temperature, following the primary cure and carried out to enhance the physical properties of the material.

powder (rubber): particles of size 1 mm or less.

preform: piece of mix of specified shape and size for the mould.

pre-former: member interposed between the extruder head and die to unify the rate of flow of rubber through the die.

press cure: vulcanisation in a mould in a press.

PRI: the abbreviation for the Plastics and Rubber Institute.

profiling machine: machine with two or more rolls of which at least one carries one or more circumferential grooves for converting rubber into strip having a predetermined contour.

proofed fabric: composite produced by proofing.

proofing: process of coating a fabric with rubber to impede penetration by a fluid usually water; the rubber-coating of such fabric.

RAPRA: the abbreviation for the Rubber and Plastics Research Association of Great Britain.

retracted spew: defect in which the rubber adjacent to the spew line shrinks below the level of the moulding, the spew line often being ragged and torn.

reverse camber: concavity of the longitudinal section of a roll.

rheometer (*Monsanto*): one type of curemeter. It is in worldwide use and has many applications as a process control instrument in addition to its normally accepted laboratory use as a measure of stiffness, scorch and functional modulus characteristics of a rubber compound. In certain cases it is even used indirectly as a comparison of dispersion by examining the reproducibility of several batches of the same material.

RMA: the abbreviation for the Rubber Manufacturers Association Inc.

roll: roller or hollow cylinder forming a major moving member of a rubber processing machine.

roll bending: adjustment to the contour of the nip formed between two rolls of a calender by bending one or both rolls.

roll deflection: bending of the moving rolls, particularly when the nip is loaded.

scorch: premature vulcanisation of a rubber mix.

screw (*scroll*): rotating member with a helical groove to propel rubber along the barrel of an extruder.

self-vulcanisation: intentional vulcanisation at or near room temperature.

skin coating: process of applying rubber to the surface of sheet material using a spreader; the layer so applied.

slab moulding: process of compression moulding in which a multi-cavity mould is charged with a single slab or sheet.

spew or flash: surplus material forced from a mould on closure under pressure.

spew line: line on the surface of a moulding at the junction of the mould parts.

spider: member with three or more spokes supporting the core in the head of the extruder.

spider line: radial line on a cross section of an extrudate corresponding to the spokes of a spider or bridge.

spread sheet: sheet made by spreading rubber dough on a support from which the sheet is finally removed.

spreader: machine for distributing rubber dough or latex on the surface of sheet material by means of a blade.

spreader chest: that part of a spreader consisting of a heated table, the function of which is to assist evaporation of solvent as the coated fabric passes over it.
spreading knife (*doctor blade*): blade used for spreading dough or latex smoothly and uniformly.
steam-pan (*autoclave*): closed vessel for treating rubber in steam usually under pressure.
stitch: the consolidation of a seam by rolling it with a stitching wheel.
stitch wheel: hand tool comprising a narrow wheel with a narrow serrated edge for stitching.
stock blender: device comprising one or more driven rollers mounted above and used in conjunction with a mill to improve blending of a mix.
strainer: machine designed to force rubber through metal gauze screens to remove extraneous matter.
strike-through: penetration of rubber coated to uncoated surface.

take-off gear: apparatus for winding material on a reel or box from a calender or spreader under controlled tension.
tee head: extruder head of T shape, to divert the flow of rubber to a direction at right angles to the axis of the screw, for direct extrusion round a core.
tension stand: assembly of large diameter rollers for tensioning fabric.
tip: detachable conical end of a centre.
topping (*skin coating*): process of applying rubber to the surface of sheet material using a calender; the layer so applied.
tracer wheel: hand tool comprising a roller with a knurled working face for consolidating a join.
transfer mould: mould for transfer moulding.
transfer moulding: moulding process in which a predetermined quantity of mix is forced into a closed heated cavity(ies) from a heated chamber integral with the mould.
treated liner: liner which has been specially treated to improve its smoothness or to ease its separation from the rubber.

vapour cure: vulcanisation by exposure to the vapour of sulphur monochloride.
variable die: die comprising two or more components each adjustable relative to the other(s).
V-block: central member of a Y-head to maintain separation of the simultaneous discharge of two extruders.
vulcanisate: main product of vulcanisation.

vulcanisation: normally irreversible process in which rubber, through a change in its chemical structure usually brought about by cross leaking, is converted to a condition in which the elastic properties are conferred, re-established, improved or extended over a greater range of temperature.

Y-head: extruder head of Y shape to direct together the simultaneous discharges from two extruders to a single die.

APPENDIX 1

SPECIFIC GRAVITY OF COMMONLY USED COMPOUND INGREDIENTS

Aluminium silicate	2·10
Ammonium carbonate	1·59
Antimony sulphide	3·00
Antimony trioxide	5·40
Asbestos	2·70
Bentonite	2·50
Bitumen	1·04
Blanc fixe	4·30
Calcium silicate	2·10
Carbon black	1·80
Carnauba wax	0·99
Casein	1·26
Ceresine wax	0·92
China clay	2·50
Cottonseed oil	0·93
Diethylene glycol	1·12
Dutrex	1·00
Ester plasticisers	1·00 (approx)
Factice ✓	1·05
French chalk (talc)	2·80
Glue	1·27
Graphite	2·40
Indene—coumarone resin	1·09
Iron oxide (red oxide)	4·80
Kaolin	2·60
Kieselguhr	2·20
Lanolin	1·08
Lead dioxide (brown)	9·40

Lime	2·19
Litharge (yellow)	9·30
Lithopone	4·30
Magnesium carbonate—light	2·21
Magnesium oxide (light oxide)	3·60
Mica dust	2·80
Mineral oil	0·91
MRX—mineral rubber	1·01
Oleic acid	0·90
Palm oil	0·80
Paraffin wax	0·90
Petroleum jelly	0·90
Pine tar	1·08
Rosin	1·07
Rosin oil	0·98
Shellac	1·15
Silica	1·95
Stearic acid	0·85
Sulphur	2·05
Titanium dioxide	3·90
Ultramarine blue	2·50
Vermilion	8·20
Whiting	2·65
Zinc oxide	5·55
Zinc stearate	1·10

Accelerators

DOTG	1·19
DPG	1·19
MBT	1·49
MBTS	1·54
TET	1·30
TMT	1·42
ZDC	1·47
ZMBT	1·64

Antioxidants/Antioxanants

Diphenyl-*para*-phenylene diamine	1·22
4-isopropylamino-diphenylamine (ZA)	1·14
Phenol/aldehyde/amine condensates (NSN)	1·08

Phenolic condensation products (EX)	1·07
Phenyl-*alpha*-naphthylamine	1·21
Phenyl-*beta*-naphthylamine	1·21

Rubber

Chloroprene (CR)	1·23
CSM	1·18
EPDM	0·86
Natural Rubber (NR)	0·93
Nitrile (NBR)	1·00
Polybutadiene	0·93
SBR	0·94
Silicone	0·98

APPENDIX 2

CONVERSION TABLES*

TEMPERATURE EQUIVALENTS OF SATURATED STEAM AT SEA LEVEL

Gauge pressure			*Approximate temperature*	
(*atmospheres*)	(*lb/in²*)	(*kg/cm²*)	(°*C*)	(°*F*)
0	**0**	0	100	212
	5	0·35	109	227
0·5	7·3	0·51	112	234
	10	0·70	115	239
1·0	14·7	1·03	121	250
	15	1·06	121	250
	20	1·41	125	258
1·5	22	1·54	127	261
	25	1·76	130	266
2·0	29·4	2·06	134	273
	30	2·11	134	274
	35	2·46	138	281
2·5	36·7	2·57	139	283
	40	2·81	141	287
3·0	44	3·09	144	291
	45	3·16	145	293
	50	3·51	148	298
3·5	51·4	3·60	149	300
	55	3·87	150	303
4·0	58·8	4·11	152	306
	60	4·22	153	307
	65	4·57	155	311
4·5	66·1	4·63	156	312
	70	4·92	158	316
5·0	73·5	5·14	159	318
	75	5·27	160	320
	80	5·62	162	324

(*continued*)

* *Courtesy:* Vulnax International Ltd

TEMPERATURE EQUIVALENTS OF SATURATED STEAM AT SEA LEVEL—*contd.*

Gauge pressure			*Approximate temperature*	
(atmospheres)	(lb/in^2)	(kg/cm^2)	(°*C*)	(°*F*)
5·5	80·9	5·68	162	324
	85	5·98	164	327
6·0	88·2	6·20	165	329
	90	6·33	165	329
	95	6·68	168	334
6·5	95·6	6·72	168	334
	100	7·03	170	338
7·0	102·9	7·23	171	340
	105	7·38	172	342
	110	7·73	173	343
7·5	110·25	7·75	173	343
	115	8·09	175	347
8·0	117·6	8·26	176	349
	120	8·44	177	351
8·5	**125**	8·78	178	352
	130	9·14	180	356
9·0	132·3	9·30	181	358
	135	9·49	182	360
9·5	**140**	9·84	183	361
	145	10·20	184	363
10·0	147	10·33	185	365
	150	10·55	186	367
	160	11·25	188	370
11·0	161·7	11·36	188	370
	170	11·95	191	376
12·0	176·4	12·40	193	379
	180	12·66	194	381
	190	13·36	196	385
13·0	191	13·43	196	385
	200	14·06	198	388
14·0	205·8	14·46	199	390
	210	14·77	200	392
15·0	**220**	15·47	202	396
	230	16·17	204	399
16·0	235·2	16·53	205	401
	240	16·88	206	403
17·0	**250**	17·57	208	406
	260	18·28	210	410
18·0	264·6	18·59	210	410
	270	18·98	211	412
19·0	**280**	19·69	213	415
	290	20·39	215	419
20·0	294	20·66	216	421
	300	21·09	217	423

TENSILE CONVERSIONS

lb/in^2	*kg/cm*^{2}	*MPa*[a]	*lb/in*^{2}	*kg/cm*^{2}	*MPa*
391	27·5	**2·7**	**650**	45·7	4·48
400	28·1	2·76	652	45·9	**4·5**
406	28·6	**2·8**	654	**46**	4·51
412	**29**	2·84	667	46·9	**4·6**
420	29·6	**2·9**	668	**47**	4·61
425	29·9	2·93	**675**	47·5	4·65
427	**30**	2·94	681	47·9	**4·7**
435	30·6	**3**	683	**48**	4·71
441	**31**	3·04	696	**49**	**4·8**
450	31·6	**3·1**	**700**	49·2	4·83
455	**32**	3·14	710	**50**	**4·9**
464	32·6	**3·2**	**725**	**51**	**5**
469	**33**	3·24	739	**52**	**5·1**
475	33·4	3·28	**750**	52·7	5·17
478	33·7	**3·3**	754	**53**	**5·2**
483	**34**	3·33	768	**54**	**5·3**
493	34·7	**3·4**	**775**	54·5	5·34
498	**35**	3·43	782	**55**	5·39
500	35·2	3·45	783	55·1	**5·4**
507	35·7	**3·5**	796	**56**	5·49
512	**36**	3·53	797	56·1	**5·5**
522	36·7	**3·6**	**800**	56·2	5·52
525	36·9	3·62	811	**57**	5·59
526	**37**	3·63	812	57·1	**5·6**
536	37·7	**3·7**	**825**	**58**	5·69
540	**38**	3·73	826	58·1	**5·7**
550	38·7	3·79	839	**59**	5·79
551	38·8	**3·8**	841	59·2	**5·8**
555	**39**	3·82	**850**	59·8	5·86
565	39·8	**3·9**	853	**60**	5·88
569	**40**	3·92	855	60·2	**5·9**
575	40·4	3·96	867	**61**	5·98
580	40·8	**4**	870	61·2	**6**
583	**41**	4·02	**875**	61·5	6·03
594	41·8	**4·1**	882	**62**	6·08
597	**42**	4·12	884	62·2	**6·1**
600	42·2	4·14	896	**63**	6·18
609	42·8	**4·2**	899	63·2	**6·2**
611	**43**	4·22	**900**	63·3	6·21
623	43·9	**4·3**	910	**64**	6·28
625	43·9	4·31	913	64·3	**6·3**
626	**44**	4·32	**925**	**65**	6·38
638	44·9	**4·4**	928	65·3	**6·4**
640	**45**	4·41	939	**66**	6·47

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in^2	kg/cm^2	MPa^a	lb/in^2	kg/cm^2	MPa
942	66·3	**6·5**	**1 200**	84·4	8·27
950	66·8	6·55	1 203	84·7	**8·3**
953	**67**	6·57	1 209	**85**	8·34
957	67·3	**6·6**	1 218	85·7	**8·4**
967	**68**	6·67	1 223	**86**	8·43
971	68·3	**6·7**	**1 225**	86·1	8·45
975	68·6	6·72	1 232	86·7	**8·5**
981	**69**	6·77	1 237	**87**	8·53
986	69·4	**6·8**	1 247	87·7	**8·6**
995	**70**	6·86	**1 250**	87·9	8·62
1 000	70·4	**6·9**	1 251	**88**	8·63
1 010	**71**	6·96	1 261	88·7	**8·7**
1 015	71·4	**7**	1 266	**89**	8·73
1 024	**72**	7·06	**1 275**	89·6	8·79
1 025	72·1	7·07	1 276	89·8	**8·8**
1 029	72·4	**7·1**	1 280	**90**	8·83
1 038	**73**	7·16	1 290	90·8	**8·9**
1 044	73·4	**7·2**	1 294	**91**	8·92
1 050	73·8	7·24	**1 300**	91·4	8·96
1 052	**74**	7·26	1 305	91·8	**9**
1 058	74·5	**7·3**	1 308	**92**	9·02
1 066	**75**	7·36	1 319	92·8	**9·1**
1 073	75·5	**7·4**	1 322	**93**	9·12
1 075	75·6	7·41	**1 325**	93·2	9·14
1 081	**76**	7·45	1 334	93·8	**9·2**
1 087	76·5	**7·5**	1 337	**94**	9·22
1 095	**77**	7·55	1 348	94·9	**9·3**
1 100	77·3	7·58	**1 350**	94·9	9·31
1 102	77·5	**7·6**	1 351	**95**	9·32
1 109	**78**	7·65	1 363	95·9	**9·4**
1 116	78·5	**7·7**	1 365	**96**	9·41
1 123	**79**	7·75	**1 375**	96·7	9·48
1 125	79·1	7·76	1 377	96·9	**9·5**
1 131	79·6	**7·8**	1 379	**97**	9·51
1 138	**80**	7·85	1 392	97·9	**9·6**
1 145	80·6	**7·9**	1 394	**98**	9·61
1 150	80·9	7·93	**1 400**	98·4	9·65
1 152	**81**	7·94	1 406	98·9	**9·7**
1 160	81·6	**8**	1 408	**99**	9·71
1 166	**82**	8·04	1 421	**100**	**9·8**
1 175	82·6	**8·1**	**1 425**	100·2	9·83
1 180	**83**	8·14	1 435	**101**	**9·9**
1 189	83·6	**8·2**	**1 450**	**102**	**10**
1 194	**84**	8·24	1 465	**103**	**10·1**

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in^2	kg/cm^2	MPa^a	lb/in^2	kg/cm^2	MPa
1 475	103·7	10·17	1 754	123·4	**12·1**
1 479	**104**	**10·2**	1 763	**124**	12·16
1 493	**105**	**10·3**	1 769	124·4	**12·2**
1 500	105·5	10·34	**1 775**	124·8	12·24
1 507	**106**	**10·4**	1 777	**125**	12·26
1 522	**107**	10·49	1 783	125·5	**12·3**
1 522	107·1	**10·5**	1 792	**126**	12·36
1 525	107·2	10·51	1 798	126·5	**12·4**
1 536	**108**	10·59	**1 800**	126·6	12·41
1 537	108·1	**10·6**	1 806	**127**	12·45
1 550	**109**	10·69	1 812	127·5	**12·5**
1 551	109·1	**10·7**	1 820	**128**	12·55
1 564	**110**	10·79	**1 825**	128·3	12·58
1 566	110·2	**10·8**	1 827	128·5	**12·6**
1 575	110·7	10·86	1 834	**129**	12·65
1 578	**111**	10·89	1 841	129·5	**12·7**
1 580	111·2	**10·9**	1 849	**130**	12·75
1 593	**112**	10·98	**1 850**	130·1	12·76
1 595	112·2	**11**	1 856	130·6	**12·8**
1 600	112·5	11·03	1 863	**131**	12·85
1 607	**113**	11·08	1 870	131·6	**12·9**
1 609	113·2	**11·1**	**1 875**	131·8	12·93
1 621	**114**	11·18	1 877	**132**	12·95
1 625	114·3	**11·2**	1 885	132·6	**13**
1 635	**115**	11·28	1 891	**133**	13·04
1 638	115·3	**11·3**	**1 900**	133·6	**13·1**
1 650	**116**	11·38	1 905	**134**	13·14
1 653	116·3	**11·4**	1 914	134·6	**13·2**
1 664	**117**	11·47	1 920	**135**	13·24
1 667	117·3	**11·5**	**1 925**	135·3	13·27
1 675	117·8	11·55	1 928	135·7	**13·3**
1 678	**118**	11·57	1 934	**136**	13·34
1 682	118·3	**11·6**	1 943	136·7	**13·4**
1 692	**119**	11·67	1 948	**137**	13·44
1 696	119·3	**11·7**	**1 950**	137·1	13·45
1 700	119·5	11·72	1 957	137·7	**13·5**
1 706	**120**	11·77	1 962	**138**	13·53
1 711	120·4	**11·8**	1 972	138·7	**13·6**
1 721	**121**	11·87	**1 975**	138·9	13·62
1 725	121·3	11·89	1 977	**139**	13·63
1 725	121·4	**11·9**	1 986	139·7	**13·7**
1 735	**122**	11·96	1 991	**140**	13·73
1 740	122·4	**12**	**2 000**	140·6	13·79
1 750	**123**	12·07	2 001	140·8	**13·8**

(*continued*)

TENSILE CONVERSIONS—*contd.*

lb/in^2	*kg/cm*^{2}	*MPa*[a]	*lb/in*^{2}	*kg/cm*^{2}	*MPa*
2005	**141**	13·83	2 305	162·2	**15·9**
2015	141·8	**13·9**	2 318	**163**	15·99
2019	**142**	13·93	2 320	163·2	**16**
2025	142·4	13·96	**2 325**	163·5	16·03
2 030	142·8	**14**	2 332	**164**	16·08
2033	**143**	14·02	2 334	164·2	**16·1**
2044	143·8	**14·1**	2 346	**165**	16·18
2048	**144**	14·12	2 349	165·2	**16·2**
2050	144·1	14·13	**2 350**	165·2	**16·2**
2059	144·8	**14·2**	2 361	**166**	16·28
2062	**145**	14·22	2 363	166·3	**16·3**
2073	145·9	**14·3**	**2 375**	**167**	16·38
2075	145·9	14·31	2 378	167·3	**16·4**
2076	**146**	14·32	2 389	**168**	16·48
2088	146·9	**14·4**	2 392	168·3	**16·5**
2090	**147**	14·42	**2 400**	168·7	16·55
2 100	147·7	14·48	2 403	**169**	16·57
2 102	147·9	**14·5**	2 407	169·3	**16·6**
2 105	**148**	14·51	2 417	**170**	16·67
2 117	148·9	**14·6**	2 421	170·3	**16·7**
2 119	**149**	14·61	**2 425**	170·5	16·72
2 125	149·4	14·65	2 432	**171**	16·77
2 131	149·9	**14·7**	2 436	171·4	**16·8**
2 133	**150**	14·71	2 446	**172**	16·87
2 146	**151**	**14·8**	**2 450**	172·3	16·89
2 150	151·2	14·82	2 450	172·4	**16·9**
2 160	**152**	**14·9**	2 460	**173**	16·97
2 175	**153**	**15**	2 465	173·4	**17**
2 190	**154**	**15·1**	**2 475**	**174**	17·07
2 200	154·7	15·17	2 479	174·4	**17·1**
2 204	**155**	**15·2**	2 488	**175**	17·16
2 218	**156**	**15·3**	2 494	175·4	**17·2**
2 225	156·4	15·34	**2 500**	175·8	17·24
2 233	**157**	**15·4**	2 503	**176**	17·26
2 247	**158**	**15·5**	2 508	176·5	**17·3**
2 250	158·2	15·51	2 517	**177**	17·36
2 261	**159**	15·59	2 523	177·5	**17·4**
2 262	159·1	**15·6**	**2 525**	177·5	17·41
2 275	**160**	15·69	2 531	**178**	17·46
2 276	160·1	**15·7**	2 537	178·5	**17·5**
2 289	**161**	15·79	2 545	**179**	17·55
2 291	161·2	**15·8**	**2 550**	179·3	17·58
2 300	161·7	15·86	2 552	179·5	**17·6**
2 304	**162**	15·89	2 560	**180**	17·65

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in²	*kg/cm²*	*MPa*[a]	*lb/in²*	*kg/cm²*	*MPa*
1 475	103·7	10·17	1 754	123·4	**12·1**
1 479	**104**	**10·2**	1 763	**124**	12·16
1 493	**105**	**10·3**	1 769	124·4	**12·2**
1 500	105·5	10·34	**1 775**	124·8	12·24
1 507	**106**	**10·4**	1 777	**125**	12·26
1 522	**107**	10·49	1 783	125·5	**12·3**
1 522	107·1	**10·5**	1 792	**126**	12·36
1 525	107·2	10·51	1 798	126·5	**12·4**
1 536	**108**	10·59	**1 800**	126·6	12·41
1 537	108·1	**10·6**	1 806	**127**	12·45
1 550	**109**	10·69	1 812	127·5	**12·5**
1 551	109·1	**10·7**	1 820	**128**	12·55
1 564	**110**	10·79	**1 825**	128·3	12·58
1 566	110·2	**10·8**	1 827	128·5	**12·6**
1 575	110·7	10·86	1 834	**129**	12·65
1 578	**111**	10·89	1 841	129·5	**12·7**
1 580	111·2	**10·9**	1 849	**130**	12·75
1 593	**112**	10·98	**1 850**	130·1	12·76
1 595	112·2	**11**	1 856	130·6	**12·8**
1 600	112·5	11·03	1 863	**131**	12·85
1 607	**113**	11·08	1 870	131·6	**12·9**
1 609	113·2	**11·1**	**1 875**	131·8	12·93
1 621	**114**	11·18	1 877	**132**	12·95
1 625	114·3	**11·2**	1 885	132·6	**13**
1 635	**115**	11·28	1 891	**133**	13·04
1 638	115·3	**11·3**	**1 900**	133·6	**13·1**
1 650	**116**	11·38	1 905	**134**	13·14
1 653	116·3	**11·4**	1 914	134·6	**13·2**
1 664	**117**	11·47	1 920	**135**	13·24
1 667	117·3	**11·5**	**1 925**	135·3	13·27
1 675	117·8	11·55	1 928	135·7	**13·3**
1 678	**118**	11·57	1 934	**136**	13·34
1 682	118·3	**11·6**	1 943	136·7	**13·4**
1 692	**119**	11·67	1 948	**137**	13·44
1 696	119·3	**11·7**	**1 950**	137·1	13·45
1 700	119·5	11·72	1 957	137·7	**13·5**
1 706	**120**	11·77	1 962	**138**	13·53
1 711	120·4	**11·8**	1 972	138·7	**13·6**
1 721	**121**	11·87	**1 975**	138·9	13·62
1 725	121·3	11·89	1 977	**139**	13·63
1 725	121·4	**11·9**	1 986	139·7	**13·7**
1 735	**122**	11·96	1 991	**140**	13·73
1 740	122·4	**12**	**2 000**	140·6	13·79
1 750	**123**	12·07	2 001	140·8	**13·8**

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in^2	kg/cm^2	MPa^a	lb/in^2	kg/cm^2	MPa
2005	**141**	13·83	2 305	162·2	**15·9**
2015	141·8	**13·9**	2 318	**163**	15·99
2019	**142**	13·93	2 320	163·2	**16**
2025	142·4	13·96	**2 325**	163·5	16·03
2 030	142·8	**14**	2 332	**164**	16·08
2033	**143**	14·02	2 334	164·2	**16·1**
2044	143·8	**14·1**	2 346	**165**	16·18
2048	**144**	14·12	2 349	165·2	**16·2**
2050	144·1	14·13	**2 350**	165·2	**16·2**
2059	144·8	**14·2**	2 361	**166**	16·28
2062	**145**	14·22	2 363	166·3	**16·3**
2073	145·9	**14·3**	**2 375**	**167**	16·38
2075	145·9	14·31	2 378	167·3	**16·4**
2076	**146**	14·32	2 389	**168**	16·48
2088	146·9	**14·4**	2 392	168·3	**16·5**
2090	**147**	14·42	**2 400**	168·7	16·55
2 100	147·7	14·48	2 403	**169**	16·57
2 102	147·9	**14·5**	2 407	169·3	**16·6**
2 105	**148**	14·51	2 417	**170**	16·67
2 117	148·9	**14·6**	2 421	170·3	**16·7**
2 119	**149**	14·61	**2 425**	170·5	16·72
2 125	149·4	14·65	2 432	**171**	16·77
2 131	149·9	**14·7**	2 436	171·4	**16·8**
2 133	**150**	14·71	2 446	**172**	16·87
2 146	**151**	**14·8**	**2 450**	172·3	16·89
2 150	151·2	14·82	2 450	172·4	**16·9**
2 160	**152**	**14·9**	2 460	**173**	16·97
2 175	**153**	**15**	2 465	173·4	**17**
2 190	**154**	**15·1**	**2 475**	**174**	17·07
2 200	154·7	15·17	2 479	174·4	**17·1**
2 204	**155**	**15·2**	2 488	**175**	17·16
2 218	**156**	**15·3**	2 494	175·4	**17·2**
2 225	156·4	15·34	**2 500**	175·8	17·24
2 233	**157**	**15·4**	2 503	**176**	17·26
2 247	**158**	**15·5**	2 508	176·5	**17·3**
2 250	158·2	15·51	2 517	**177**	17·36
2 261	**159**	15·59	2 523	177·5	**17·4**
2 262	159·1	**15·6**	**2 525**	177·5	17·41
2 275	**160**	15·69	2 531	**178**	17·46
2 276	160·1	**15·7**	2 537	178·5	**17·5**
2 289	**161**	15·79	2 545	**179**	17·55
2 291	161·2	**15·8**	**2 550**	179·3	17·58
2 300	161·7	15·86	2 552	179·5	**17·6**
2 304	**162**	15·89	2 560	**180**	17·65

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in^2	kg/cm^2	MPa^a	lb/in^2	kg/cm^2	MPa
2566	180·5	**17·7**	2827	198·9	**19·5**
2575	**181**	17·75	2830	**199**	19·52
2581	181·6	**17·8**	2842	199·9	**19·6**
2588	**182**	17·85	2844	**200**	19·61
2595	182·6	**17·9**	**2850**	200·4	19·65
2600	182·8	17·93	2856	200·9	**19·7**
2602	**183**	17·95	2858	**201**	19·71
2610	183·6	**18**	2871	**202**	**19·8**
2616	**184**	18·04	**2875**	202·1	19·82
2625	184·6	**18·1**	2885	**203**	**19·9**
2631	**185**	18·14	**2900**	**204**	**20**
2639	185·6	**18·2**	2915	**205**	**20·1**
2645	**186**	18·24	**2925**	205·7	20·17
2650	186·3	18·27	2929	**206**	**20·2**
2653	186·7	**18·3**	2944	**207**	**20·3**
2659	**187**	18·34	**2950**	207·4	20·34
2668	187·7	**18·4**	2958	**208**	**20·4**
2673	**188**	18·44	2972	**209**	**20·5**
2675	188·1	18·44	**2975**	209·2	20·51
2682	188·7	**18·5**	2986	**210**	20·59
2688	**189**	18·54	2987	210·1	**20·6**
2697	189·7	**18·6**	**3000**	**211**	20·69
2700	189·8	18·62	3001	211·1	**20·7**
2702	**190**	18·63	3015	**212**	20·79
2711	190·7	**18·7**	3016	212·2	**20·8**
2716	**191**	18·73	**3025**	212·7	20·86
2725	191·6	18·79	3029	**213**	20·89
2726	191·8	**18·8**	3030	213·2	**20·9**
2730	**192**	18·83	3043	**214**	20·99
2740	192·8	**18·9**	3045	214·2	**21**
2744	**193**	18·93	**3050**	214·4	21·03
2750	193·4	18·96	3057	**215**	21·09
2755	193·8	**19**	3059	215·2	**21·1**
2759	**194**	19·03	3072	**216**	21·18
2769	194·8	**19·1**	**3075**	216·2	**21·2**
2773	**195**	19·12	3086	**217**	21·28
2775	195·1	19·13	3088	217·3	**21·3**
2784	195·8	**19·2**	**3100**	**218**	21·37
2787	**196**	19·22	3103	218·3	**21·4**
2800	196·9	**19·3**	3114	**219**	21·48
2801	**197**	19·32	3117	219·3	**21·5**
2813	197·9	**19·4**	**3125**	219·7	21·55
2816	**198**	19·42	3128	**220**	21·58
2825	198·6	19·48	3132	220·3	**21·6**

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in²	*kg/cm²*	*MPa*[a]	*lb/in²*	*kg/cm²*	*MPa*
3 143	**221**	21·67	3 413	**240**	23·54
3 146	221·3	**21·7**	3 422	240·7	**23·6**
3 150	221·5	21·72	**3 425**	240·8	23·62
3 157	**222**	21·77	3 427	**241**	23·63
3 161	222·4	**21·8**	3 436	241·7	**23·7**
3 171	**223**	21·87	3 441	**242**	23·73
3 175	223·2	21·89	**3 450**	242·6	23·79
3 175	223·4	**21·9**	3 451	242·8	**23·8**
3 185	**224**	21·97	3 455	**243**	23·83
3 190	224·4	**22**	3 465	243·8	**23·9**
3 200	**225**	22·06	3 470	**244**	23·93
3 204	225·4	**22·1**	**3 475**	244·3	23·96
3 214	**226**	22·16	3 480	244·8	**24**
3 219	226·4	**22·2**	3 484	**245**	24·03
3 225	226·7	22·24	3 494	245·8	**24·1**
3 228	**227**	22·26	3 498	**246**	24·13
3 233	227·5	**22·3**	**3 500**	246·1	24·13
3 242	**228**	22·36	3 509	246·8	**24·2**
3 250	228·5	**22·4**	3 512	**247**	24·22
3 256	**229**	22·46	**3 525**	247·8	**24·3**
3 262	229·5	**22·5**	3 527	**248**	24·32
3 271	**230**	22·56	3 538	248·9	**24·4**
3 275	230·3	22·58	3 541	**249**	24·42
3 277	230·5	**22·6**	**3 550**	249·6	24·48
3 285	**231**	22·65	3 552	249·9	**24·5**
3 291	231·5	**22·7**	**3 555**	**250**	24·52
3 300	**232**	22·75	3 567	250·9	**24·6**
3 306	232·6	**22·8**	3 569	**251**	24·62
3 313	**233**	22·85	**3 575**	251·4	24·65
3 320	233·6	**22·9**	3 581	251·9	**24·7**
3 325	233·8	22·93	3 583	**252**	24·71
3 327	**234**	22·95	3 596	**253**	**24·8**
3 335	234·6	**23**	**3 600**	253·1	24·82
3 342	**235**	23·05	3 610	**254**	**24·9**
3 350	235·5	**23·1**	**3 625**	**255**	**25**
3 356	**236**	23·14	3 640	**256**	**25·1**
3 364	236·6	**23·2**	**3 650**	256·6	25·17
3 370	**237**	23·24	3 655	**257**	**25·2**
3 375	237·3	23·37	3 669	**258**	**25·3**
3 378	237·7	**23·3**	**3 675**	258·4	25·34
3 384	**238**	23·34	3 683	**259**	25·4
3 393	238·7	**23·4**	3 697	**260**	**25·5**
3 400	**239**	23·44	**3 700**	260·1	25·51
3 407	239·7	**23·5**	3 711	**261**	**25·6**

(continued)

TENSILE CONVERSIONS—*contd.*

lb/in²	*kg/cm²*	*MPa*[a]	*lb/in²*	*kg/cm²*	*MPa*
3725	261·9	25·68	3987	280·5	**27·5**
3726	**262**	**25·7**	3996	**281**	27·56
3740	**263**	25·79	**4000**	281·2	27·58
3741	263·2	**25·8**	4002	281·5	**27·6**
3750	263·7	25·86	**4010**	**282**	27·66
3754	**264**	25·89	4016	282·5	**27·7**
3755	264·2	**25·9**	**4025**	**283**	27·75
3768	**265**	25·99	4031	283·6	**27·8**
3770	265·2	**26**	4038	**284**	27·85
3775	265·4	26·03	4045	284·6	**27·9**
3783	**266**	26·09	**4050**	284·8	27·92
3784	266·2	**26·1**	4053	**285**	27·95
3797	**267**	26·18	4060	285·6	**28**
3800	267·2	**26·2**	4067	**286**	28·05
3811	**268**	26·28	**4075**	286·5	**28·1**
3813	268·3	**26·3**	4081	**287**	28·15
3825	**269**	26·38	4089	287·6	**28·2**
3828	269·3	**26·4**	4095	**288**	28·24
3839	**270**	26·48	**4100**	288·3	28·27
3842	270·3	**26·5**	4103	288·7	**28·3**
3850	270·7	26·55	4110	**289**	28·34
3854	**271**	26·58	4118	289·7	**28·4**
3857	271·3	**26·6**	**4125**	**290**	28·44
3868	**272**	26·68	4132	290·7	**28·5**
3871	272·3	**26·7**	4138	**291**	28·54
3875	272·5	26·72	4147	291·7	**28·6**
3882	**273**	26·77	**4150**	291·8	28·61
3886	273·4	**26·8**	4152	**292**	28·64
3896	**274**	26·87	4161	292·7	**28·7**
3900	274·2	26·89	4166	**293**	28·73
3900	274·4	**26·9**	**4175**	293·5	28·79
3910	**275**	26·97	4176	293·8	**28·8**
3915	275·4	**27**	4181	**294**	28·83
3925	**276**	27·06	**4190**	294·8	**28·9**
3929	276·4	**27·1**	4195	**295**	28·93
3939	**277**	27·17	**4200**	295·3	28·96
3944	277·4	**27·2**	4205	295·8	**29**
3950	277·7	27·24	4209	**296**	29·03
3953	**278**	27·26	4219	296·8	**29·1**
3958	278·5	**27·3**	4223	**297**	29·13
3967	**279**	27·36	**4225**	297·1	29·13
3973	279·5	**27·4**	4234	297·8	**29·2**
3975	279·5	27·41	4238	**298**	29·22
3982	**280**	27·46	**4250**	298·8	**29·3**

(*continued*)

TENSILE CONVERSIONS—*contd.*

lb/in²	*kg/cm²*	*MPa*[a]	*lb/in²*	*kg/cm²*	*MPa*
4 252	**299**	29·32	4 437	**312**	**30·6**
4 263	299·9	**29·4**	**4 450**	312·9	30·68
4 266	**300**	29·42	4 451	**313**	**30·7**
4 275	300·6	29·48	4 465	**314**	30·79
4 277	300·9	**29·5**	4 466	314·2	**30·8**
4 280	**301**	29·52	**4 475**	314·6	30·86
4 292	301·9	**29·6**	4 479	**315**	30·89
4 294	**302**	29·62	4 480	315·2	**30·9**
4 300	302·3	29·65	4 494	**316**	30·99
4 306	302·9	**29·7**	4 495	316·2	**31**
4 309	**303**	29·72	**4 500**	316·4	31·03
4 321	**304**	**29·8**	4 508	**317**	31·09
4 325	304·1	29·82	4 509	317·2	**31·1**
4 335	**305**	**29·9**	4 522	**318**	31·19
4 350	**306**	**30**	**4 525**	318·2	**31·2**
4 364	**307**	**30·1**	4 536	**319**	31·28
4 375	307·6	30·17	4 538	319·3	**31·3**
4 379	**308**	**30·2**	**4 550**	319·9	31·37
4 394	**309**	**30·3**	**4 550**	**320**	31·38
4 400	309·4	30·34	4 553	320·3	**31·4**
4 408	**310**	**30·4**	4 565	**321**	31·48
4 425	**311**	**30·5**			

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[a] 1 MPa (megapascal) = 10·197 kgf/cm^2 = 1 N/mm^2 = 1 MN/m^2.

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