THESIS ON

CYCLISED RUBBER

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By

PUSHKARAKSHAN M.
DEPARTMENT OF POLYMER SCIENCE & RUBBER TECHNOLOGY
UNIVERSITY OF COCHIN
COCHIN - 682022

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Being a student of the B.Tech Course in Rubber Technology I had occasions to discuss the manufacture of modified rubbers with entrepreneurs in this field. The impression I gathered is that Cyclised Rubber, one of the modified forms of rubbers, will be a prospective raw material for many applications especially when petroleum based synthetic resins are becoming scarce and costlier. This is specially true with natural rubber producing countries. Eventhough cyclised rubber is commercially manufactured in many countries it is not manufactured in India. Hence it was thought a deep probe in to the subject will be of interest.

This thesis in the form of a dissertation is an attempt on the above objective.

In preparing this dissertation I have received help from various people from my department and other institutions.

I am deeply indebted to Dr.A.P.Kuriakose, Reader, Dept. of Polymer Science & Rubber Tech., for his excellent guidance in each and every step in preparing this thesis. I express my whole-hearted thanks to him. Dr.D.Joseph Francis, Professor & Head, Dept. of Polymer Science & Rubber Tech., was very much helpful to me during my work. I extend my sincere thanks to him. Mr.E.V.Thomas, Dy. Director and Mr. Baby Kuriakose, Rubber Technologist, RRII, Kottayam, for their valuable suggestions and helps which was really fruitful to me. I express my sincere thanks to them.

My classmates and other staff members have rendered their valuable cooperation and help to me which made my work easier. I remember all of them with thanks.

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PUSHKARAKSHAN . M

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CHAPTER-I

INTRODUCTION

Under the action of heat and especially in the presence of acidic substances, natural rubber is transformed into isomeric resinous substance of reduced unsaturation known as cyclised rubber[1]. This change is accompanied by increase in softening point, density and refractive index and internal cyclisation is proposed[2], since the increase in the indicated physical properties are consistent with already known effects of cyclisation of terpenes (eg. dihydromyrcene)[3].

The first isomer of this kind was prepared by Harries in 1910 by treating natural rubber with con.sulphuric acid[4]. Later many other chemicals were used for bringing about cyclisation. These products were resinous materials with reduced unsaturation

Cyclisation can be effected by either (a) heat (b) reductive dehydrogenation of rubber halides (c) by the action of halides of amphoterric metals or (d) by acidic catalysts.

The propertiesof fully cyclised[4] rubbers prepared by different methods do not differ much. There is no reason to believe that widely different structural features result from varrious methods.

The various methods of preperation of cyclised rubber may be briefly discussed here. The methods of manufacture of commercial importance will be discussed in detail in Chapter IV.

Thermal Cyclisation:-

Heating can induce cyclisation in natural rubber. The reaction is a slow one and takes hours for completion. Usually the rubber is heated in a solvent[5] at 250 - 300°C. Volatile degradation products are continously removed either by reduction of pressure or by passing a stream of inert gas. It is usually found that 30 - 40 % of rubber remains unchanged in this cyclised modification. It is notable that under similar conditions of temperature and time the same amount of conversion was observed even in the absence of a solvent.

Heat cyclised rubber is a pale coloured powdery materials. It is soluble in a number of solvents but is insoluble in alchol and acetone. The cryoscopic determination of the molecular weight indicates a value of 2,000 to 2,500.

Cyclisation through Reductive Dehydrohalogenation:-

Dehydrohalogenation of rubber hydrochloride or hydrobromide with alkaline agents at 100 - 150°C gives iso rubber; (iso rubber contains displaced but undiminished unsaturation) which by reductive dehydrogenation with zinc dust and acid gives cyclised rubber.[2] The cyclised rubber produced by this method is much similar to the heat cyclised product. Their molecular weight ($\overline{Mn}$) is in between 2,300 - 14,500 depending on conditions of reaction.

Cyclisation by Halides of Amphoteric Metals:-

When stannic chloride is added to a rubber solution under an inert atomosphere at room temperature a coloured compound is formed. It is believed to be a complex of rubber with the halide[6,7].~~6, 7~~. The complex can be decomposed rapidly by the addition of alcohol or water. The cyclised rubber is precipitated from the solution as an amorphous white powder by adding excess alcohol. Another method of recovering the cyclised rubber is by removing the solvent by steam. Similar reactions occur with ferric chloride, antimony pentachloride, aluminium trichloride and titanium tetra chloride. It was also found that Friedel-Crafts catalyst were of little use as the cyclising agents.

Hydrated chlorostannic acid has been used to promote cyclisation. It demands higher temperatures. This process is of commercial value as the reagent is capable of cyclising rubber both in solution and bulk. In a typical process the rubber is refluxed in solution ~~wt~~ with 10 p.h.r. (by w/w) of hydrated chlorostannic acid. In the case of the bulk method 10 p.h.r. of chlorostannic acid is incorporated into the rubber on a two rall mill. Then the product is heated for 2 to 5 hours at a temperature of 130 - 150°C.

The product is an amorphous powder soluble in rubber solvents. The solubility is much dependent on the conditions of reaction. The product is readily soluble in solvents provided the premastication step is avoided and suitable protection with antioxidants is given against oxidative degradation. The product usually contains a little chlorine (usually about 1%) together with stannic oxide. The product has a higher density of 1.02 gm/c.c. But after purification the product will have a specific gravity of 0.96 to 0.98.

Cyclisation by acidic reagents:-

It may be noted that this class of reagents has found much application in the manufacture of cyclised rubber. This class includes con.sulphuric acid and its organic derrivatives of general structure R-SO_2-X where R is an organic group and X is a hydroxyl or halogen. (the most important examples are p - tolune sulphonic acid and its chloride) Phenols containig sulphuric[9] acid or phosphoric acid[10] are also used as cyclising agents. Besides these materials, hydrogen fluoride, trichloro acetic acid and acidic esters can also be used. Boron triflurride in acetic acid ~~and Boron trifluoride~~ and various halogen derrivatives of phosphorous have also been used as cyclising agents.

For the cyclisation of natural rubber in the bulk the most important reagents are sulphoric acids, sulphonyl chlorides and sulphuric acid. About 10 p.h.r. of these reagents is capable of bringing cyclisation in a reasonable time at temperatures of 120 - 130°C. These reagents may be incorporated into the bulk of rubber on a mixing mill. The liquid reagents like con. sulphuric acid is conveniently incorporated after mixing with an inert filler. The mixture of cyclising agent and rubber is then heated at 125 - 145°C for a period of 1 - 4 hours.

The nature of the product obtained depends upon the degree of cyclisation which in turn is determined by the temperature reached by the mass and the time of heating. Usually the products obtained can be classified into three types.[11]

1. Resilient or elastic materials similar to vulcanised rubber . (Degree of cyclisation about 50)
2. Hard, tough and plastic materials resembling balata and gutta percha (Degree of cyclisation 50 - 70)
3. Hard, tough or sometimes brittle and friable products resembling shellac (Degree of cyclisation greater than 70)

By far p - tolune ~~sulph~~ sulphonic acid is the most important and economic cyclising agent for natural rubber in bulk.

The method of cyclising rubber on a mixing mill was developed by the Rubber Stiching Co. & Dunlop Rubber Co.[12], the rubber on the mill and heating the mixture in an oven for several hours at temperature around 150°C. The research works carried out at Rubber Stiching Co. made further improvements. The first modification came as the internal mixer was found to be more convenient to carry out the reaction. This resulted in a more homogenous product and good temperature control. The second modification was the addition of small amounts of a strongly absorbing white filler of small particle size (eg. Aerosil). This has resulted in strong accelerating effect on the reaction which made it possible to obtain complete cyclisation of even lower grades of natural rubber.

Another important development in this field is marked by the use of low nitrogen content natural rubber.[13] It was found that the nitrogen content and time of cyclisation have an inverse relation. This is taken advantage in the commercial manufacture of cyclised rubber. Using papain as the latex coagulant low Nitrogen rubber is prepared.

Cyclised rubbers can be prepared from rubber latex also. But the main difficulty is that the latices are highly unstable towards acidic materials and most of the efficent cyclising agents are acidic materials. The latex stage cyclisation is attractive as it dose not need any solvents or the solvent recovery system. This will help to reduce the unit cost of production.

For carrying out cyclisation in the latex stage, the latex is to be stabilised properly. Anionic stabilisers are of little use here, but it can stabilised with cationic stabilisers such as Cetyl trimethyl ammonium bromide[14] or lauryl pyridinium chloride. Non-ionic stabilisers[15] such as polyethylene oxide condensate can also be used.

Con. sulphuric acid is the preferred cyclising agent for natural rubber latex. To obtain a reasonably good rate of reaction a fairly high concentration of sulphuric acid in the serum is needed. A concentration of at least 70% w/w is a must for appreciable reaction rate. Kinetic studies reveal that the reaction rate is directly dependent on the concentration of acid in the serum and the temperature of reaction. The reaction is highly exothermic especially at early stages and cooling is necessary to prevent run away conditions. (The manufacturing details are discussed in Chapter IV.)

The most promising use of cyclised rubber as the reinforcing resin has created interest in developing Cyclised Rubber Master Batches; which are readily used for applications like shoe soling. Usually CRMB is a 50/50 mixture of natural rubber and cyclised rubber.[16].

Before the commercialisation of High Styrene Resins the cyclised rubber found much application in rubber compounding as the stiffening agent. It may be noted that many of the petrochemical based resins can substitute most of the applications of cyclised rubber. But the use of p-toluene sulphonic acid and low nitrogen content natural rubber made it possible to manufacture cyclised rubber at compatitive prices. Also the increasing cost of petroleum based resins offers good prospects for the manufacture of cyclised rubber.

In the countries where natural rubber is produced in abundance and the synthetic materials are imported this material find immense potential. The cost of production will be comparable with that of synthetic resins.

Different cyclised rubbers which were in commercial use earlier are briefly reviewed below:[4]-

Isolac was developed and marketed by E.I. Dupont & Co. Their main use was as the stiffening resin in rubber compounds. They improved the stiffness and toughness at normal atmospheric temperatures. It is believed that Isolac was manufactured by the action of β-napthol on natural rubber.

Plioform another industrially prepared cyclised rubber was manufactured by treating natural rubber with chlorostannic acid. The important application of plioform was to make tough ebonite mouldings of pale colour.

Another variety of cyclised rubber of commercial importance is manufactured by using borontrifluoride as the cyclising agent. These materials find use to bond unvulcanised rubber to metal. These are also used in paints.

Pliolite another solution cyclised natural rubber developed in U.S.A. also found use in adhesives and paints. Plastonal Ltd., England also marketed a solution cyclised natural rubber under the trade name plastoprene.

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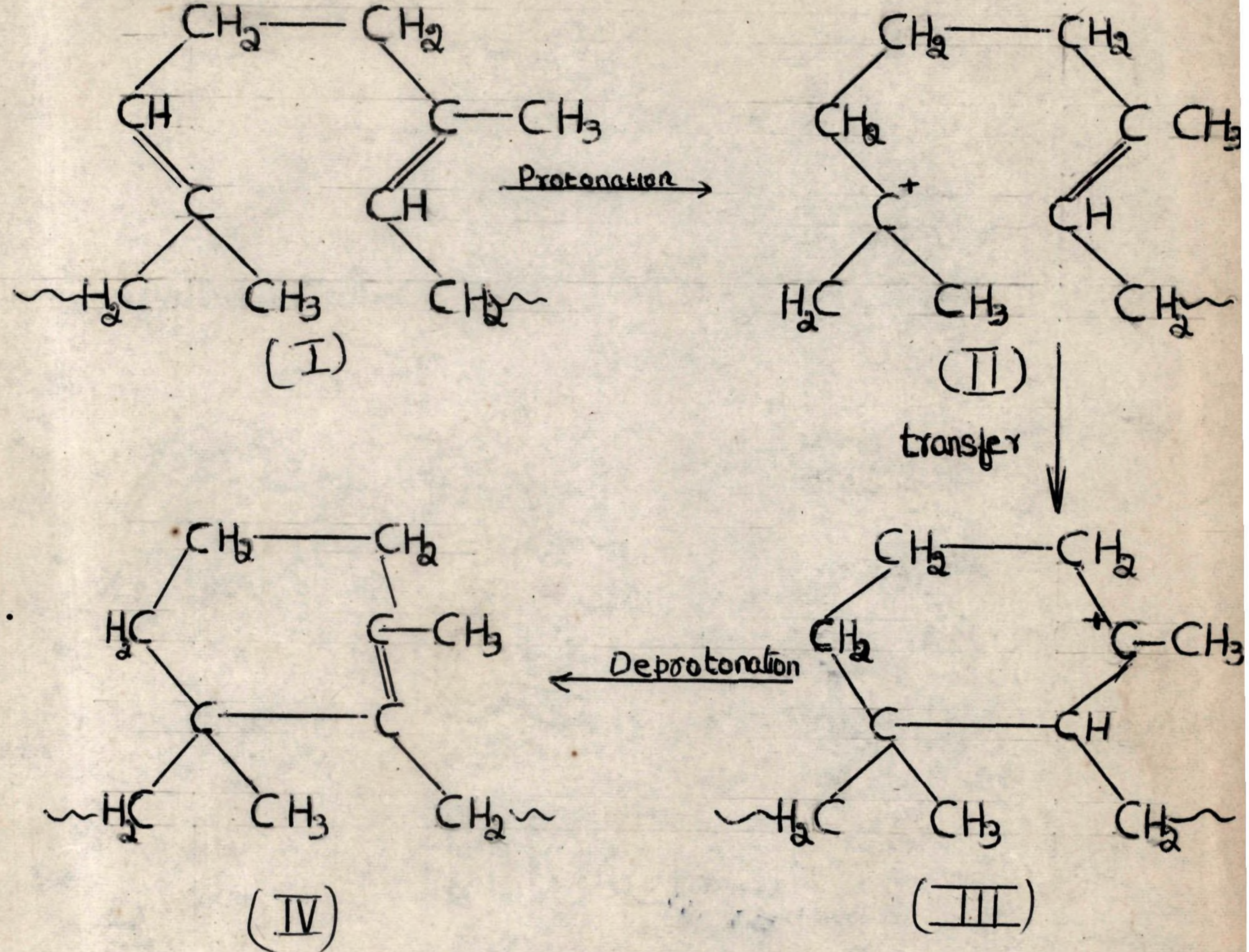
CHAPTER-II

CHEMISTRY & TECHNOLOGY

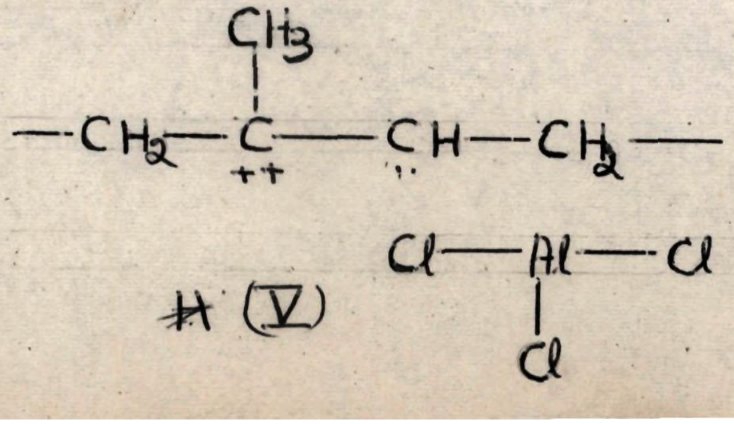
In this chapter the chemistry of cyclisation of rubbers are discussed. Also mentioned are some of the technological significance of cyclised rubbers.

There has been much speculation as to the nature of the cyclisation reaction in rubbers. It is abundantly clear that it is an ionic reaction requiring the presence of a proton donor; the reaction is quite unresponsive to reagents which influence free radical reactions, and ~~up~~ upto the present time no method has been described for cyclising ~~of~~ rubber by a free radical mechanism.

From the readiness with which dihydromyrcene (a compound structurally similar to natural rubber) is cyclised by acidic reagents[1] there is no reason to suppose that the course of reaction is different in rubber, and there is general agreement that cyclisation proceeds by protonation to produce (II) and addition of the resulting carbonium ion to an adjacent double bond to form a six membered ring (III), as has been proposed for dihydromyrcene[2].



Cyclisation by Friedal-Crafts reagents may involve carbonium ion formation in a complex of the type (V) or protonation.



~~H~~ (V)

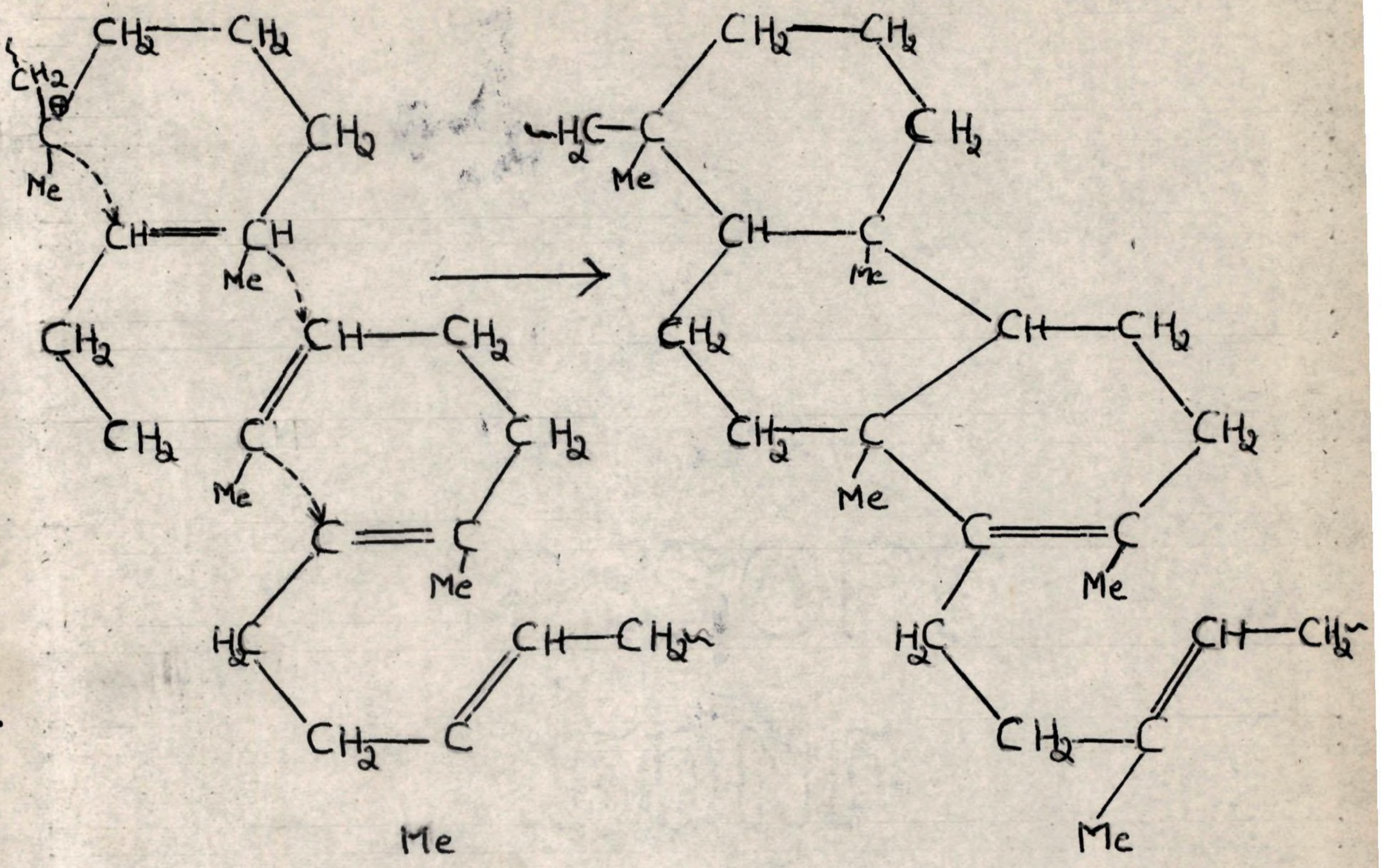
as above by action of a co-catalyst such as is usually required in ionic ~~plym~~ polymerisation promoted by these reagents[3].

$$H_2O + SnCl_4 \longrightarrow H-\underset{\underset{H}{|}}{O}\rightarrow SnCl_4 \rightleftharpoons \overset{\oplus}{H} + HO\overset{\ominus}{Sn}Cl_4$$

$$H_2SnCl_6 \rightleftharpoons \overset{\oplus}{H} + H\overset{\ominus}{Sn}Cl_6$$

Cyclisation is propageted to further adjacent units (VI) until terminated by a deprotonation step (VII)[4]. This formulation of cyclised rubber is one of polycondensed cyclohexane rings and it is necessary to assume that sequences of such condensed rings are distributed between segments of uncyclised polyisoprene to account for residual unsaturation of cyclised rubber, which is substantially greater than one double bond in the terminal ring of each cyclised sequence.

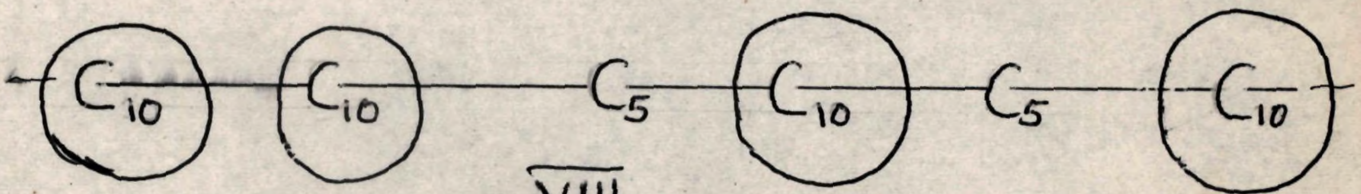
The kinetics of rubber cyclisation in latex are , however more in accordance with the deprotonation step (IV) completing a cyclisation involving two isoprenic units at a time[5,6] rather than a propagating reaction involving sequences of propagating units as formulated in (VI)



VI

VII

A direct consequence of such a reaction, involving at random adjacent pairs of isoprene units is that the ultimate composition of fully cyclised rubber must be a 'copolymer' of C_{10}- cyclic structures and isolated C_5 units eg:-



VIII

Such a radom co-polymer should contain 13.5% of the isolated C_5 units[7] and if it can be demonstrated unambigously that the unsaturation remaining in fully cyclised rubber corresponds to this composition the above cyclisation paired up all of the ~~availa~~ available C_5 - units in cyclic structures each containing one double bond the unsaturation of the original polyisoprene would clearly be halved, as indeed happens with low molecular analogue dihydromyrcene. The statistical distribution of cyclised and isolated units requires that the unsaturation shall be 56.8% of the original rubber instead of 50% expected if each cyclised unit contains one double bond. The polycondensed structure (VIII) on the otherhand, would retain only a small proportion of the original unsaturation of the rubber when cyclisation is pushed to completion. Supporting evidence for these structures is therefore critically dependent on the correct determination of the unsaturation of cyclised rubber and unfortunately this cannot be determined with complete certainly by the usual method of halogen addition owing to substitutive side reaction. The IR spectrum does not assist very much in the elucidation of cyclised rubber structure[8]; some features which are indicative of $C = CH_2$ groups have been found to survive ozonolysis. The spectrum gives some indication of residual unsaturation of polyisoprenic pattern but does not exclude the presence of unsaturation of the tetra substituted ethylene type as formulated in (IV), there are some features in common with the spectrum of 1:2 dimethylcyclohex-1 ene[9].

Some of the earlier workers ~~on cyclisation~~ obtained, by halogen addition, unsaturation values corresponding to the presence of only one double bond in four or five cyclic units, and they accordingly proposed polycyclic structures.[10, 11] More recently further evidence for a polycyclic structure has been obtained by estimating the unsaturation by addition of hydrogen chloride[4] which revealed only 17% of the original rubber unsaturation. On the other hand, there are several pieces of independent evidence for the statistical copolymer (VIII) based on units of structure (IV)these are

1. Dilatometric experiments using latex showed that the reaction was more conistent with statistical cyclisation law, than with a first order equation for the survival of stranded units.[5,6].

2. The most reliable unsaturation value obtained by addtion of iodine chloride[12] was 57% of that of original rubber.

3. The reaction of phenyliododichloride, which adds chlorine quantitatively to double bends, with latex cyclised rubber gave additive chlorination corresponding to an unsaturation value 58.3% of that of rubber.[13]

4. The unsaturation of samples of heat cyclised and acid cyclised (latex process) rubber estimated by quantitative ozone uptake were respectively 55 & 58% of that of rubber[14].

5. Oxidation with chromic acid gave 25 - 30% acetic acid instead of 66% given by rubber, thus indicating half unsatuation of the rubber.[15]

Some rate abnormalities observed in the kinetics of latex cyclisation include an induction period of reduced rate, probably related to diffusion effects. A small volume change subsequent to cyclisation may reflect a prototropic shift of the double bond and this may have some bearing on the structural features indicated by IR spectrum[16].

Con.sulphuric acid is effectively used for cyclisation in the latex stage. A fairly high concentration of acid is required in the serum. For a reasonable rate of reaction at least 70% w/w acid is required in the serum. The detailed kinetic studies has resulted in the following equation[16].

$$\log_{10} K = 6 + 0.17\, C - 7150 / T$$

C is the concentration of sulphuric acid expressed % by wt.
T is the absolute temperature and
K is the rate constant.

At 100° C cyclisation is reasonably complete within two hours when 70% acid is used. From the equation it can be seen that either one percentage increase in 'C' or an increase of 3°c in 'T' increases the rate by 50%. So it is necessary to control the rate carefully. It also follows that conditions can be established for carrying out the process of cyclicing rubber to any desired level. Partially cyclised rubbers having difference in properties from both fully cyclised and uncyclised rubbers have also been prepared.

The extent of cyclisation can be determined by calculating the density of the product. A reference chart of the densities at different degrees of cyclisation is prepared. Knowing the densityof the sample the degree of cyclisation can be found out from the chart. Density increases with degree of cyclisation. The unreacted natural rubber has a density of 0.92 to 0.94 and the fully cyclised rubber has a density of around 0.98 to 0.99.

Another method of determining the degree of cyclisation is the determination of unsaturation which is more easily evaluated by determining iodine number. The raw natural rubber has one unsaturation per isoprenic unit and iodine number is
373.6 about 375.

It will be appropriate to discuss the technological significance of cyclised rubber also in this chapter.

Cyclised rubber is an isomeric material of natural rubber with a softening point of 120 to 130°C. Just like other raw rubbers cyclised rubber also will have to be mixed with other chemicals before converting it in to useful products of industrial applications.

Other ingredients can be mixed with cyclised rubber either in a two roll mixing mill or in an internal mixer. Mill mastication gives rise to some problems[17]. Milling at higher temperatures results in oxidative breakdown even in presence of antioxidants. The plasticised cyclised rubber has a tendency to adhere to the mill rolls and hence an internal mixer gives better results. The mill mixing is usually done at 95 - 100°C. In two roll mills cyclised rubber is put on the mill first and when a band is formed at 70°C other elastomers or other ingridents are added.

Cyclised rubber is a thermoplastic material and hence dose not need any curatives or acceleraters. But they undergoes oxidative ~~ag~~ ~~aging~~ ageing and hence antioxidants are to be used. Nonox NS is an antioxidant commonly used with cyclised rubber. No reinforcement is obtained by using reinforcing fillers. But there are a number of plasticizers used[18] with cyclised rubber. They include Tritolyl phosphate, trixylyl phosphate, benzyl-n-butyrate, triphenylphosphate, benzyl benzoate and p-(chloromethyl)xylene).

When cyclised rubber is used as a reinforcing resin in rubber compounding it has to be properly blended with the elastomer. The good compatability of cyclised rubber with natural and synthetic rubbers is an added advantage here. In a typical blending and compounding with natural rubber~~x~~, the N.R. is masticated slightly and the previously sheeted cyclised rubber is added and blended with minimum breakdown. Then fillers and the curatives are added. When an internal mixer is used the cyclised rubber is first blended with natural rubber and then half the filler and zinc oxide are added followed by the remainder of filler, zinc oxide and other ingreidents with the exception of sulphur which is added at the end of the cycle.

After dumping from the mixer the compound is passed twice through a tight nip on the two roll mill and sheeted off. 24 hours rest is given prior to resheeting the compound and curing[18].

Cyclised rubber can be processed in injection, compression and transfer moulding techniques. Eventhough cyclised rubber is considerably stiffer than standard crepe or sheet rubbers, the compound has good flow characterstics and readily flows in the mould.

The compounds containing cyclised rubber can be compression moulded in the same way as other elastomers are compression moulded. Cyclised rubber for injection moulding has also been investigated.[19] Cyclised rubber masterbatch in the powder form was suitable for injection moulding. However it has a tendency to degrade and to give an offensive smell during ~~injection moulding~~ processing. It possesses good extrusion characterstics also. Thin walled tubings can be cured in chalk without fear of collapse. Curing may be done in steam or with hot air; but best results are obtained in the hydraulic press.

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CHAPTER - III

PROPERTIES AND USES

In this chapter the properties and uses of cyclised rubber are discussed.

Cyclised rubber has a density of 0.98 to 0.99 gm/c.c.[1] The refractive index is in the range of 1.53 to 1.54[2]. The resin has a softening point at 120 - 130°C. The molecular weight depends upon the method of preperation. It usually ranges from 2,300 to 14,500. ($\overline{Mn}$). The properties of cyclised rubber are directly related to the degree of cyclisation. But most of the properties are not much dependent upon the method of preperation in the case of fully cyclised rubber.

Depending upon the degree of cyclisation[3] mainly three types of cyclised rubber are obtained.

1) Resilient or elastic substance similar to vulcanised rubber.
2) Hard, tough, ~~heat~~ and plastic~~s~~ variously resembling balata, hard balata and gutta percha.
3) Hard, tough or sometimes brittle and friable products resembling shellac.

The cyclised rubber is compatible with a number of plastisizers and is soluble in most of the rubber solvents. It can be incorporated with coumorone-indene resin, paraffins, estergum, resin, chlorinated oils etc. The flammability of cyclised rubber is less than that of raw rubber and decreases with increased degree of cyclisation.

Cyclised rubber is most widely used in shoe soling. In the shoe soling it gives good abrasion resistance, and excellent wear properties. It posseses good compatablity with natural rubber and synthetics. ~~But NSR gives some problems in mixing with natural rubber.~~

In the following table different proportions of NR and cyclised rubber is compared in a shoe soling compound.

Table : 1

Ratio of cyclised rubber to natural rubber by wt.	0:10	1:9	2:8	3:7	4:6	5:5
Cure time at 120°C in minutes	60	75	75	75	75	75
Tensile strength kg/cm^2	399	276	214	173	103	74
Elongation at break %	995	830	650	540	480	270
300% modulas kg.	6	13	32	55	66	--
Hardness Shore A	31	40	51	58	72	87
Shore elastisity	80	75	82	42	24	21
Permanent set 24 hours at 200% at 20°C measured 24 hours after moulding.	3.5	9.5	5.5	41	74	61

It can be seen that the ratio between 2:8 and 3:7 is most suitable. Usually in soling a ratio of 1:3 is used.

In table No.2 a comparison is made between cyclised rubber and high styrene resin for shoe soling and in table 3 the physical properties of these two, compounded for same hardness are compared.[5]

Table : 2 Physical properties of vulcanizates reinforced with high styrene resin and cyclised rubber.

Cyclised rubber masterbatch (3:1)	44.0	---
High styrene resin masterbatch (3:1)	--	44.0
RSS	89.0	89.0
Silica	15.5	15.0
Zinc oxide	3.5	5.5
Stearic acid	2.0	2.0
Process oil	7.0	7.0
PBN	1.0	2.0
TMTD	0.1	0.1
MBTS	0.6	0.6
Triethanolamine	1.0	1.0
Cumarone Indene Resins	1.5	1.5
Crumb	90.0	90.0
Cure time at 140°C (min)	7.5	12.5
Tensile strength (kgs/cm^2)	109.8	99.9
Modulus at 300% elongation (kgs/cm^2)	70.7	74.4
Hardness (IRHD)	86.0	80.0
Tear strength (kgs/cm^2)	49.4	32.3

It can be seen that the physical properties such as hardness, modulus, tensile strength and split tear resistance are higher in samples containing cyclised rubber ~~than high styrene resins, cyclised rubber is thus more efficient than high styrene resin, when precipitated silica is used as the reinforcing filler.~~

<u>Table : 3</u>

	Cyclised rubber compound	H.S.R. compound
Ratio of HSR or cyclised rubber to NR	1:3	1 : 3
Cure time at 142°C in min.	10	10
Tensile strength kg/cm^2	275	275
Elongation at break %	480	540
Tensile strength at 100°C	70-80	116
Elongation at break % at 100°C.	470	440
300% modulus kg/cm^2	152	100
Hardness shore °A	60	60
Shore elasticity	70	64
Permanent set	5	10
~~Permanent set~~ Tear resistance kg/cm^2	110	56
Abrasion mm^3/kg.	1.5	2.0
Flex cracking (1000 cycles)	19	25
Cut growth (1000 cycles)	80	58
Brittle point	-54°C	-50°C
Lupke resilience		
20°C	75	65

50°C	83	72
80°C	83	77
100°C	85	60
After cooling and again testing		
20°C	77	69

High resilence combined with high modulus is the striking result of cyclised rubber compound. Tensile strength at high temperature (100°C) and elongation break are less in cyclised rubber compared to HSR, while lower heat build up and better tear resistance are advantages. It was also found that Mullins effect is less with cyclised rubber reinforced stock.

The cyclised rubber readily mixes with natural or synthetic rubbers. While high styrene resins offer some problem in mixing with natural rubber. The compounds containing cyclised rubber are easily processing and require less acceleration than analogous compounds based on HSR[7]. In comparison to HSR, cyclised rubber exhibits a higher softening temperature which gives better form stability in cure of extruded articles. Difficult moulding operations are also simplified by the inclusion of 5 - 10 p.h.r. of cyclised rubber as the process aid. Lower compression set is attained compared to HSR, and M.C. soles are reported to give exceptionally good split tear resistance. Compounds having hardness 99° BS are readily attainable with cyclised rubber and can be processed in conventional rubber machinery.

HSR compounds show marked softening at appreciably lower temperatures than cyclised rubber compounds ~~and cyclised rubber~~ which give~~s~~ higher shear modulas. Whereas HSR softens at temperatures only a little above room temperature, the cyclised rubber shows no appreciable softening below 80°C. The superior compression set figures obtained with cyclised rubber in comparison with HSR compounds and its higher softening point, no doubt account for the superior resistance to spread shown by cyclised rubber during wear. Under the laboratory test conditions cyclised rubber compounds have less cutgrowth resistance than HSR compounds.

Typical formulations for shoe soling and other industrial applications based on cyclised rubber ~~has~~ are given below[9]:-

Table : 4 Typical formulation for Heavy duty Industrial Roller (Non Black)

	p.h.r.
CRMB	70
RSS	30
Zno	5.0
Stearic acid	1.0
Nonox NS	1.0
C.B.S.	0.8
Sulphur	2.5
Titanium dioxide	5.0

Cure time at 142°C (minutes)	20
Hardness IRHD	75

Table : 5 Typical formulation~~s~~ for shoe soling and physical properties based on CRMB

	Solid	Micro porous	Semi blown
	p.h.r.	p.h.r.	p.h.r.
CRMB	45	30	75
RSS	55	70	25
Aluminum silicate	60	40	--
Calcium silicate	--	--	60
Zinc oxide	5	5	5
Stearic acid	2	2	2
Yellow ochre	3	3	3
Red ochre	0.2	0.2	0.2
CI resin	--	15	--
Nonox HFN	1.0	1.0	1.0
Agretic white	0.8	0.8	0.8
CBS	0.7	0.7	0.7
Valcacle BN	--	4.0	2.0
Sulphur	2.5	2.5	2.5
Cure time at 153°C (minutes)	8	10	8
~~Densit~~ Density	1.24	0.5	0.94
Compression set	6.0	--	--
Hardness IRHD	93	44	85
Split tear kg.	--	20	10
Cut growth	5/150	8/400	8/400

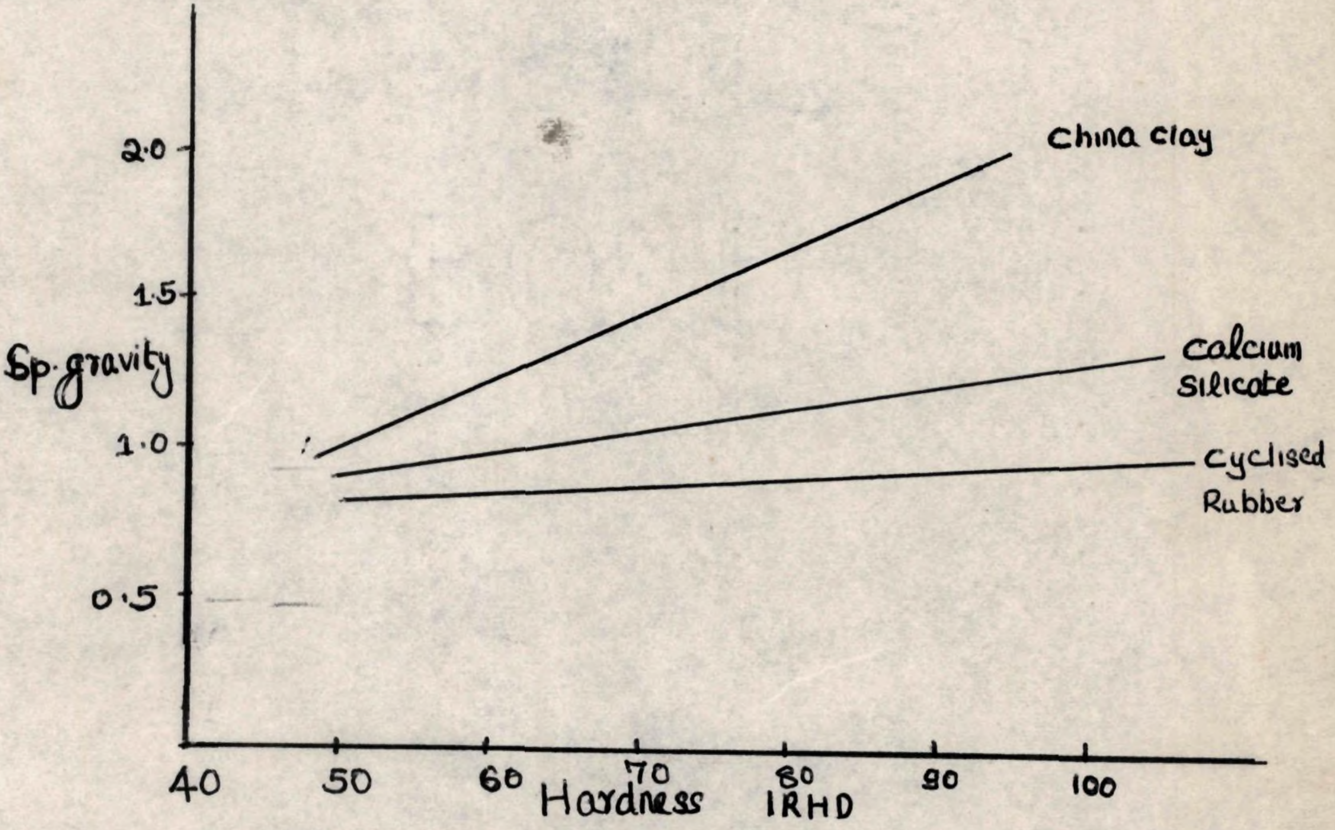
Table : 6 Hard Moulding Formulations

	1st grade p.h.r.	2nd grade p.h.r.
CRMB	100	75
WRT reclaim	--	25
MPC black	15	15
China clay	75	--
Whiting	--	75
Zinc oxide	5	4.0
Stearic acid	2.0	2.0
Nonox EXN	0.5	1.0
TMT	1.0	--
MBT	1.0	1.5
DPG	--	0.5
Sulphur	1.5	2.0
Cure time at 162°C in minutes	5	5
Hardness IRHD	99	99

Total rubbe
87.5 onl

Cyclised rubber is usually used in the form of Cyclised Rubber Master Batches. A brief mention of manufacture of CRMB has already been made earlier and it may be noted that the following discussion is mainly on cyclised rubber / N.R. blends.

Although cyclised rubber is considerably harder than standard crepe or sheet rubbers the master batch readily softens on the mill and can be blended with rubber in all proportions. Mixing can be done with standard rubber machinery and compounds flow readily in the mould. This particular property shows good advantage when compared with rubber compounds of similar hardness containing mineral fillers. Hard compounds of low density can be prepared[8] with the use of cyclised rubber as can be seen from the following chart.



As a filler Cyclised rubber is superior to calicum silicate and precipitated calcium carbonate but slightly inferior to aluminiam silicate, when the physical properties such as ~~harness~~ hardness and tensile strength are compared as shown in the following charts.

Table : 7

Filler	Hardness	Tensile strength kg/cm^2
Precipitated Calcium Carbonate	45	270
	60	185
	70	75
Calcium Silicate	45	270
	60	225
	80	150
	100	60
Cyclised rubber	45	270
	60	240
	70	210
	90	150
	100	115
Aluminium Silicate	45	270
	60	250
	70	240
	80	200
	90	185
	100	140

Table : 8 100% modulus in kg. Vs Hardness:

	Hardness	Modulus
Cyclised rubber	40	9
	50	11
	60	15
	70	25
	80	50
	90	85
	100	110
Precipitated Calcium Carbonate	40	9
	50	10
	60	20
	70	22
	80	25
Aluminum silicate	40	9
	50	10
	60	11
	70	13
	80	15
	90	22
	100	25

Calcium Silicate	40	9
	50	10
	60	12
	70	15
	80	20
	90	30
	100	50

Microcellular solings with ultra fine pore structure can be successfully prepared by using CRMB with suitable nitrogen forming blowing agents. Soles of density 0.5 to 1.0 gm/c.c. are obtained by this method.

In the fields other than soling, CRMB can be used to advantageous in the production of semi-rigid articles. One particular outlet which is proving successful is with non-black industrial rollers. These are being satisfactory used with plastic extruding plant, outliving a conventional rubber roller with the additional advantage that the absence of carbon black avoids any staining of the extruded plastic rods.

For rigid moulding CRMB has an advantage over other resin reinforcing materials due to its higher softening point. A pure gum compound will produce vulcanisates of 98° shore A in a short curing cycle and in addition to this, mineral fillers can be incorporated to produce products of even greater rigidity.

Table : 9 Typical formulations for extruded articles:

	p.h.r.	p.h.r.	p.h.r.
CRMB	100	100	100
Zno	5	5	5
Stearic acid	1	2	2
Nonox WSL	1	1	1
Uretea white	1	-	-
EPC	-	20	15
MBTS	-	-	1.0
TMT	-	-	0.5
CBS	-	0.7	--
Sulphur	2.5	2.5	2.5
China clay	-	-	60
Colour	1.0	-	-
Cure at 140°C min.	30	20	10

The suggested compound will extrude readily and thin walled tubing can be cured in chalk without fear of collapse. Simple moulding can also be prepared from the above compounds without difficulty but intricate and thin walled mouldings are liable to be less successful owing to distortion when removing from the hot mould.

Thus ~~we have~~ it can be seen that the biggest outlet for cyclised rubber is as a reinforcing filler. It is used mainly in M.C. rubber products and to a lesser extent in hard rubber products such as hard ~~rubber~~ soles, battery tops and pipe joints. The resin reinforcement is useful when light weight is an important criterion, for example in beach slippers, microcellular products and shoe soles.

Some of the uses of cyclised rubber in the paint industry may also be examined. A paint is usually manufactured from the different components such as pigments, binder~~s~~ or film former, solvent and other additives[10].

Cyclised rubber can be used in emulsion and enamel paints as the binder in place of synthetic lattices. Due to its solubility in white spirit, it is widely used in smooth finishes, particularly where brush application is required or the paint has to be applied in an enclosed space.

Stable inorganic compounds such as titanium dioxide, oxides of zinc, lead, iron, chromates of lead, zinc, barium and several others ~~inorganic compound~~ are used as pigments in paints. Pigments give the required opacity and covering. Extenders such as clay, whiting and silica are used in paints to cheapen the product as well as to provide the required viscosity for brushing and prevent settlement of heavy pigments.

Binder is at least equally important to bind together the pigment particles and to hold them on to the surface. The other additives in paint are usually the dispersing agents, wetting agents, plasticizers, stabilisers, fungicides, thickening agents and thixotropic agents ~~etc~~. The liquid phase used is water or organic solvents, or mixture of solvents.

The use of cyclised rubber is as the binder. NR latex is the first choice as the binder. But unmodified latex had the following problems:-

1) The latex coagulates during the addition of pigments or extenders.
2) Even when the paint is prepared by using a very high concentration of stabilisers, it is not possible to store or use due to its poor mechanical and chemical stabilities.
3) Paint film will be ~~to~~ rubbery
4) Adhesion to surface is not satisfactory.
5) Low oxidation resistance.

These can be rectified to a great extent by modifying the latex by prevulcanisation, graft copolymerisation or by cyclising.

Cyclised rubber is suitable for the preperation of quick drying chemical resistant paints. It is soluble in petroleum hydrocarbons and a 1:1 mixture of Low Aromatic White Spirit and High Aromatic White Spirit. These are the most widely used solvents for cyclised rubber in the manufacture of paints.

Cyclised rubber can also be used in road marking paints.[4] The advantages of using cyclised rubber as the binder in road marking paints are:-

1. Quick drying characteristics, so minimum traffic blocking.
2. Weather resistance.
3. Chemical and water resistance.

4. Abrasion resistance.

One of the draw-backs is its poor solvent resistance. Solvent resistance can be improved by incorporating a small percentage of drying oil alkyd. A typical formulation is given below:-

Table : 10 Formulation for road marking paint

Cyclised rubber	100 kg.
Rubber seed oil alkyd	18 "
Titanium dioxide	58.00 "
Coloured pigment	1.5 "
Kaolin	70 "
Solvent (HAWS:LAWS 1 : 1)	60 gallons.

The alkyd resin also acts as a plasticizer for the cyclised rubber resin. Additional plasticization by compounds present in the bitumen from the road may also be expected.

Due to its chemical resistance cyclised rubber is suitable for use in anticorrosive paints and also in machinery paint. The other additives are adjusted for the end use. Floor paints are prepared by mixing cyclised rubber varnish with other additives and iron oxide pigment.

The viscosity of cyclised rubber in solvent is less than that of chlorinated rubber and therefore it is easier to make paints having high solid contents and greater build using cyclised rubber[11]. Cyclised rubber is soluble in aliphatics and this has led to its adoption in a much wider range of paints and printing inks than chlorinated rubber which is soluble only in solvent blends rich in aromatic contents. Paints based on cyclised rubber can be formulated to resist quite high temperature, much higher than ~~tak~~ that of chlorinated rubber which begins to breakdown rapidly above 140°C.

Typical formulations for different types of paints are given below:-

Table : 11

	a	b	c	d	e
Cyclised rubber	100	100	100	100	100
Red lead	133	--	--	--	--
Zinc oxide	33	--	--	--	40
Raw tung oil	5	--	--	--	--
White spirit	300	300	300	300	300
Turpentine	--	--	--	200	100
Aluminium powder or paste	33	--	--	100 (added just before use)	--
Kieselghur	20	--	--	--	100
Carbon black	--	30	30	--	--
Titanium dioxide	--	--	--	--	160
* ~~hour drying~~ linseed oil	--	--	15	--	--

a - Redlead Primer.

b - Corrossion Resistant Black.

c - Weather Resistant Black.

d - Aluminum paint for use on iron and steel.

e - Flat white wall paint.

Also given below are formulations for Heat Resisting Enamel, Chemical Resisting Varnish, and Red oxide Floor Enamel.[6]

Heat Resisting Enamel:-

	%
25% Titanium dioxide	36
Chromium oxide	4
Cyclised rubber	40
White spirit	20

Chemical Resisting Varnish (Plasticisied)

	%
Cyclised rubber	66
Aroder 1254	17
White spirit	17

Red Oxide Floor Enamel:-

	%
Cyclised rubber	48
Thickened wood oil	4
Red oxide	12
Asbestine	14
White spirit	22

Satisfactory white paint[13] can be prepared by ball milling cyclised rubber (450 gm.), Titanium dioxide (65 g), Dibutyl phthalate as plasticiser (2.5 g) and 1:1 mixture of xylene and Mineral Turpentene (1,500 gm) as solvent. Good floor paint is also made by incorporating Orvwal iron oxide pigment into cyclised rubber varnish using a mortar and pestle.

50 gm of cyclised rubber ~~and~~ 25 gm of pigment and 100 gms of solvent, the 1:1 mixture of xylene and mineral tarpentane is used in this case.

Cyclised rubber is used in large quantity for adhesive purposes also .In practice various proportions of cyclised rubber/ natural rubber is used. It is found that a blend of 70/30 gave a very good general purpose adhesive[14].

The property of cyclised rubber to have low solution viscosity even at very high solid content is taken advantage here too. Solutions of cyclised rubber can be usedas basic material for preperation of adhesives for joining a number of different types of surfaces such as rubber, wood, leather, glass, metals, ceramics and PVC each other or their combinations.

Cyclised rubber is used in bonding of rubbers[16]. Of the many methods of cyclisation those which yield a chlorine-containing product are the most effective here and makers of ~~proper~~ proprietery brands offer special types for use with NR and with synthetic rubbers.

For bonding metals the solution of the cyclised rubber, generally with a small amount of plasticizer such as dibutyl phthalate, is applied to the clean metal surface and allowed to dry. Neither the thickness of the coating nor the time of drying seen to be highly critical. Spraying is a good method of application; but if a brush is used it should be applied quickly and lightly. The rubber compound is then cured in contact with the coated metal. Vulcanisation may be brought about in steam or even hot air, but the best results are obtained in the hydraulic press, using either a simple 2 piece mould or a transfer mould.

NR & synthetics may be bonded but butyl offers some problem, ~~it~~ which can be overcome by high sulphur content (5 - 100 parts). The use of cyclised rubber is thus a very convenient means of bonding and one capable of further development. Bond-strength upto 1000 p.s.i. may be obtained. CR gives thermoplastic bonds. The best type of CR to be used depends upon the nature of rubber to be bonded.

Cyclised rubber is used in several types of inks also. In printing ink rapid drying is brought about because solvent in ink penetrates into the paper, leaving the resin and pigment on the surface, where they dry very rapidly. This phenomenon induced by cyclised rubber, is utilised in letter press and offset inks[12].

The printing ink based on cyclised rubber is prepared with easily soluble type. In a typical recipe, one part by weight of cyclised rubber, ~~and~~ 2 parts by weight of titanium dioxide and 1.5 parts by weight of toluene is used. The viscosity is adjusted later by further addition of the solvent. This ink was used to print on cellophane under factory condition and found to be good.

The stenciling inks based on cyclised rubber has also been developed. They are found to be superior to water based inks in Water resistance and Abrasion resistance.

Cyclised rubber can also be used in offset, litho, letter press, silkscrene, copper plate and photograviecre inks[15].

Some of the other general uses to which cyclised rubber is put may be briefly discribed as follows:-

Paper~~s~~ coated with cyclised rubber has excellent moisture resistance. The formulation includes a little antioxidant. The coated papers are used for wrapping food stuffs to retain their moisture and for making bags to hold hygroscopic chemicals such as salt and lime.[12]

Cyclised rubber powder prepared by latex process is readily dispersable in water to form a dispersion. This type of dispersion~~s~~ of cyclised rubber is used for stiffening dipped or foamed latex articles.

By melting cyclised rubber with paraffin wax Pleowax is obtained.[12] This has been used to protect foodstuffs which are dipped into the molten mixture.

A cyclised rubber based coating for coconut shells used for latex collection is reported to increase the quality of sheet and crepe rubbers in the rubber plantation industry.[15]

Cyclised rubber is a potential row material for electrical insulating lacquers. Carbon fibers can also be manufactured from cyclised rubber after fabricating it to improve its flow characterstics.[15] Some plasticizers are added for this purpose. Cyclised rubber based compounds can also be used as shock resistent plastics. A typical compound contains 70 parts cyclised rubber and 30 parts of raw rubber as a plasticizer with normal amounts of fillers and curatives. The articles made are hard and glossy and very resistent to shock and blows. The fields of application include shock helmets, golf ball covers, wash basins etc.[17]

Another most promising field of use of cyclised rubber is for imitation leather goods.[17] A typical compound would consist 70 parts of rubber 30 parts of cyclised rubber with white fillers and normal amount of curatives.

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CHAPTER - IV

PREPARATION/MANUFACTURE

Cyclised rubber is manufactured in latex stage as well as in dry state. In the dry state manufacture p-toluene sulphonic acid is the most important commercially viable cyclising agent now available.

The credit goes~~t~~ to Rubber Stiching Co. and Dunlop Rubber Co. for developing the process of cyclisation in the bulk. Their method was to mill mix the p-tolune sulphonic acid with rubber and the mixture was heated in an oven for several hours at 150°C. Two far-reaching developments later in this field were the entroduction of banbury mixing and the usage of silica. The banbury mixing gives good dispersion and temperature control. The addition of small amounts of a strongly absorbing white filler of small particle size (eg. Aerosil) results in strong accleration of the reaction. These made it possible to obtain complete cyclisation of even lower grades of rubber in appreciably less time.

The different grades of p-tolune sulphonic acid gave different rates of cyclisation. These differences in activities are attributed to the water content of the acid. Drying the acid in vaccum (1 mm Hg at 120°C) gave strong increase in activity.

In a typical banbury cycle the rubber, acid and silica are put into the internal mixer simultaneously. The time is noted at the moment these ingridents are added. The initial temperature is maintained at 120 to 140°C. The reaction being strongly exothermic the temperature rises during cyclisation and falls again after the reaction ceases. In normal practice the highest temperature reached is 180°C.

The progress of the reaction can be studied by noting the energy uptake during the whole process. This is achieved by coupling an amperometer to the driving motor. During mixing period the energy uptake should be moderate and constant, otherwise slipping will take place and the mixing will not be efficent. When appreciable cyclisation has taken place and the exothermic heat of reaction is removed by cold water, the energy required will increase highly with sharp fluctuations indicating that the mixture has stiffened.

By far the best indication of the progress of reaction however is the amount of ~~the~~ gas evolved.[1] About 3 - 4 minutes after filling the banbury a steady stream of gas will be produced and the flow of steam and cold water should be regulated so as to keep the rate of gas formation constant.

Cyclisation on the mill is also practiced. The rubber is masticated and a smooth band is formed. Then the p-tolune sulphonic acid and precipitated silica are added and fully incorporated by giving minimum number of cutting. Then the sheet is cut off and heated in an oven.

In the cyclisation of natural rubber with p-tolune sulphonic acid, the following variables are found to influence[2].

p-toluene sulphonic acid concentration	(A)
Temperature of heating the mixed stock	(B)
Duration of heating	(C)
Amount of precipitated silica	(D)

In a statistical analysis of cyclisation with p-toluene sulphonic acid, Baby Kuriakose et.al[2] found that the effects of A, B, C and D on the cyclisation of natural rubber was significant at 1% level. A, B, C and D intracted significantly between themselves at 1% level. They found that at a level of 5 p.h.r. of A the iodine value (ie the measure of unsaturation and hence degree of cyclisation) was same irrespedive of temperature of heating. At 10 and 15 p.h.r. of A significant changes were observed and the lowest iodine value was obtained at 140°C.

At the level of 5 and 10 p.h.r. of A the minimum iodine value was obtained for heating period of 4 hours. For all temperatures and heating periods the iodine value was lowest with 15 p.h.r. of A. 7.5 p.h.r. of D gave lowest iodine value than other levels of D. From these they concluded that the compound containing 15 p.h.r. p-toluene sulphonic acid and 7.5. p.h.r. of precipitated silica at a temperature of 140°C for 6 hours was ideal to get cyclised rubber.

The main draw back of the method is that at the present level of prices the product obtained by this method will cost more than high styrene resin for which cyclised rubber can be a substitute.

Cyclised rubber resin that are used in many paints and adhesives is made by conducting the cyclisation reaction in presence of excess phenol containing a little sulphuric or phosphoric acid, under conditions causing little or no combination of phenol with resin. The cyclised rubber obtained is comparatively of low molecular weight owing to severe degradation occuring during its preperation.

Natural rubber in the form of ribbed smoked sheet is masticated on a mill and then dissolved in benzene in a mild steel steam jacketted vessel. The amount of benzene used is about ten times the weight of rubber used. The rubber solution is then pumped to a leadlined mild steel, steam jacketted reactor. This reactor is provided with a condenser. Sulphuric acid and phenol are now added to cyclise the rubber and the mixture is refluxed. The solution is pumped to another leadlined vessel provided with a steam sprayer. Steam is sprayed into the solution and vapours of benzene, phenol and steam are condensed with a condenser. This condensate is treated further to recover benzene and phenol.

The cyclised rubber is ground and washed with 2% sodium hydroxide and hot water to remove the impurities.

The product is now ground in a roller mill to get the cyclised rubber in the powder form[3]. The process eventhough expensive gives such special grades of cyclised rubber which are of use in expensive paints and inks.

Another economically feasible method for the production of cyclised ruber was developed by Rubber Research Institute of Sri Lanka[4]. At present a few plants are reported to be producing cyclised rubber in that country using this method helping them to do away with the import of high styrene resin into that country. This method is based on the cyclisation of natural rubber containing very low percentage of nitrogen using p-toluene sulphonic acid as the cyclising agent.

The effect of nitrogen content on the cyclisation reaction can be understood from Table-1. The nitrogen content of natural rubber is very much dependent upon the method of coagulation and other methods of processing done on the latex.

Processing of natural rubber in to different forms of low nitrogen rubbers is detailed in Annexures A1, A2,& A3.

Table - 1 Effect of Dilution, Xylyl mercaptan and Nitrogen content on Cyclisation[5]:

The latex treated with 0.25% Nonidet P 40 and coagulated with 0.25% Papain.

D.R.C.	Nitrogen % wt. on rubber	Xylyl mercaptan % wt. on rubber	Time for completion of cyclisation in sec.	Comments
35	0.22	--	1800	Low degree of cyclisation.
35	0.22	1.0	1800	Low degree of cyclisation.
18	0.18	--	360	High degreeof cyclisation
18	0.18	1.0	260	High degree o cyclisation
9	0.13	--	150	High degree o cyclisation.
9.	0.13	1.0	135	High degree o cyclisation. Vigorous reaction.
9	0.12	1.0 (Added to latex)	130	High degree o cyclisation. Vigorous reaction.

The effects of various reagents on cyclisation of papain coagulated low nitrogen content natural rubber is given in the following table.

Table - 2 Effect of Inhibitors and Activators on Cyclisation of Papain coagulated Rubber[5]

Treatment prior to coagulation with 0.25% papain	Chemicals added to dry papain coagulated rubber	~~Rubber~~ Time for completion of reaction in sec.	Comments
No fraction taken 1:1 dilution	--	High	Low degree of cyclisation.
10% fraction 1:1 dilution	--	400	High degree of cyclisation.
10% fraction taken 1 : 1 dilution	Sod. sulphate 1% on rubber	High	Low degree of cyclisation.
10% fraction taken 1 : 1 dilution	Sod. bisulphate + 1% on rubber	High	Low degree of cyclisation.
10% fraction taken 1:1 dilution	Xylyl mercaptan 1% on rubber	310	High degree of cyclisation.
10% fraction taken 1 : 1 dilution	Xylyl mercaptan 2% on rubber	300	High degre of cyclisation. Vigorous reactio
10% fraction taken 1 : 1 dilution	2, 6 ditert-butyl p-cresol 1% on rubber.	360	High degree of cyclisation.
10% fraction taken 1:1 dilution. Nonidet P40 at 0.25% on rubber	--	300	High Degree of cyclisation vigorous reaction.
10% fraction taken 1 : 1 dilution. Nonidet P40 at 0.25% on rubber	Xylylmercaptan 1% on rubber	250	Good melt flow High degree of cyclisation and vigorous reaction.

The low nitrogen rubber is cyclised by p-toluene sulphonic acid on a two roll mill. The manufacturing details are described below:-

Raw material requirements

The basic raw materials required are deproteinsied natural rubber prepared as given in the Annexure A1, A2, A3; p-toluene sulphonic acid and a little of calcium oxide.

Machinery:-

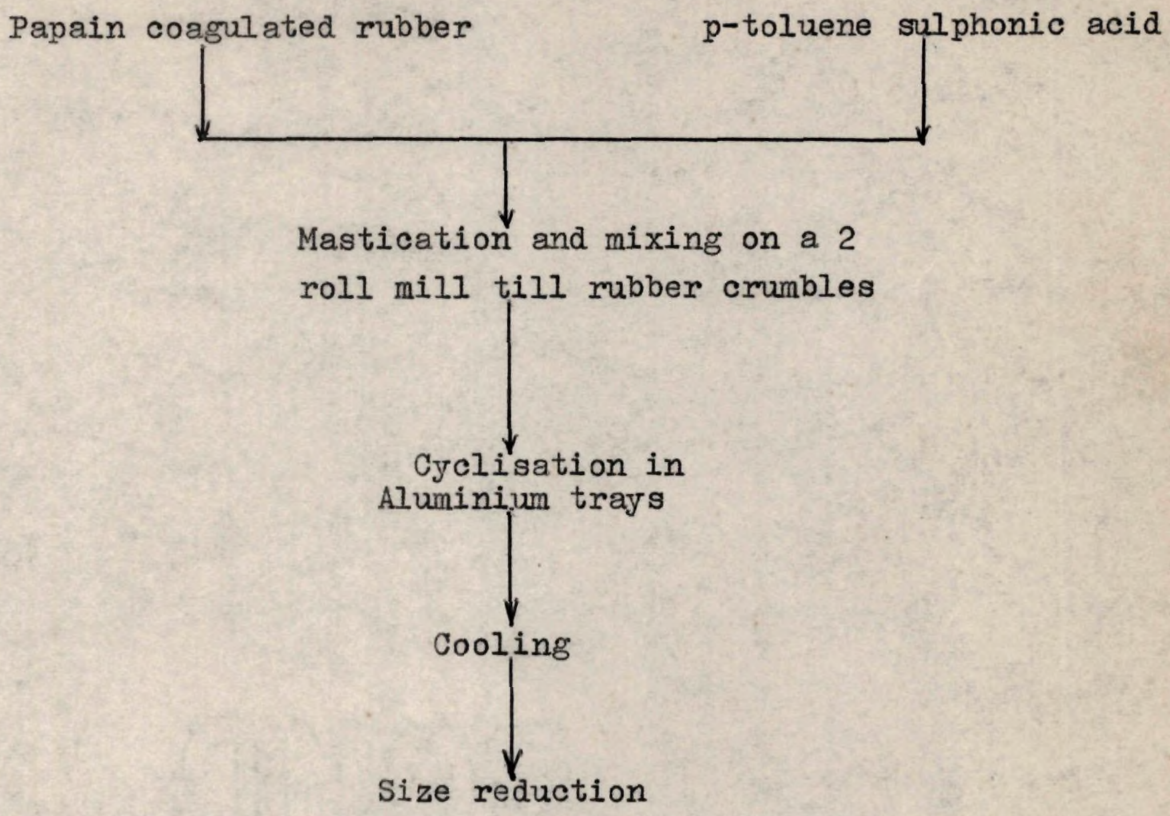
The most important machinery involved is a two roll mixing mill. A smooth roll mill of chilled cast iron is used. The rollers should be made corrossion resistant. Grooved roll mill~~s~~ also is needed.

Process details:-

Cyclisation is effected by milling the rubber with 10 parts of para-toluene sulphonic acid. The mixing is continued until the rubber crumbles into small pieces. In general 30-45 minutes milling is necessary. The crumbs are then made into a loose sheet and kept in aluminium trays for autocyclisation to occur.[4]

During cyclisation rubber melts and flows with copious evolution of fumes which contain mainly water-vapour and small amounts of decomposition products from rubber and para-toluene sulphonic acid. The cyclised rubber thus obtained is cooled and passed through grooved roll mill for size reduction.

The process may be represented as:-



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Excess ~~acid~~ acid present in the product has to be neutralised. Products used in reinforcing application is neutralised by incorporating calcium oxide. In the case of solution applications, the excess acid is removed by washing first with water followed by ammonium hydroxide or sodium carbonate and then finally with water.

Cyclisation time:-

Cyclisation time is the time for completion of reaction from it begining. The cyclisation time is an important factor in cyclisation of rubbers. It is a function of the nature of rubber used, the activators or inhibators present, the temperature of reaction etc. The tables 2 gives the influence of various inhibitors and activators on cyclisation time[5]. ~~The table 1 gives the influence of xylyl mercaptan used as an activator of cyclisation and nitrogen content on cyclisation.~~

The feasibility study for starting a small scale rubber unit for the production of cyclised rubber using p. toluene sulphonic acid is also included in this chapter. The report on this is included in different sections of Annexure II. A compartive study of the cost of cyclised rubber and high styrene resin for which cyclised rubber is a substitute is also included.

The latex stage cyclisation has been mentioned earlier. The latex is suitably stabilised with cationic or preferably with non-ionic stabiliser to prevent coagulation by addition of acids. Con. sulphuric acid is the prefered cyclising agent in latex. To obtain a reasonably good rate of reaction a fairly high concentration of sulphuric acid in the serum is needed. A concentration of at least 70% w/w is a must for appreciable reaction rate. Kinetic ~~farxa~~ studies reveal that the reaction rate is directly dependent on the concentration of acid in the serum and the temperature of reaction. The reaction is highly exothermic especially at early stages and cooling is necessary to prevent run away conditions.

The high dosage of acid in the serum demands that the latex should be of highest possible concentration. This is the bottleneck of its commercial feasibility. Even with highly concentrated latex the amount of sulphuric acid needed is substantial, and its disposal presents a considerable problem. Even at the most favourable conditions 1.5 kgs. of sulphuric acid is required per kg. of cyclised rubber produced. Attempts has been made to lower the acid concentration at higher temperature and at super atmospheric pressure. Another experiment was to use a small amount of acid and to concentrate the acidefied latex by evaporation. None of these methods is commercially employed.

In a laboratory preparation[6] 134 gms of natural rubber latex of 58% DRC is stablised with 1.5% Emulphor O. To this 161 gms of con. sulphuric acid is added to a point where the serum contained 75% w/w of acid. The reaction is carried out by heating at 80°C for 6 hours and the mixture is then diluted with 3 times its volume of water. The cyclised rubber is thus seperated.

~~No details regarding the commercial cyclisation of latex was available.~~ After the reaction the latex may be flocculated by pouring into aqueous alchol. The latex stabilised by non-ionic stabiliser may be flocculated by pouring into a considerable excess of boiling water. After filtration, washing and drying the cyclised rubber is obtained in the form of fine powder. The fineness of these particles causes its isolation costly and very laborious. It is easily redispersed in water to form a dispersion of cyclised rubber which has been used for stiffening dipped or foamed latex articles.

The most promising use of cyclised rubber as the reinforcing resin has created intreast in developing Cyclised Rubber Latex Master Batch~~s~~. Usually CRMB is a 50/50 mixture of natural rubber and cyclised rubber.

The cyclised rubber masterbatch is prepared in the latex stage by blending the cyclised rubber latex and ordinary latex in the correct proportion[6]. For the 50/50 CRMB the rubber content of both of the lattices should be same.

The natural rubber latex is cyclised as discussed previously. This cyclised latex is ~~now~~ mixed with concentrated latex of same DRC. The ordinary latex should be suitably stablised against the acid contained in the cyclised rubber latex. [In practice the natural rubber latex is stabilised with non-ionic stabiliser. The most preffered stabilisers are ~~a~~ mildly cationic stabilisers made by condensation of ethylene oxide with ~~to~~ higher alkyl ammines.] Now the CRMB is flocculated, washed and dried as discussed earlier. The acidity is nutralised by adding sodium hydroxide after flocculation.

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References:-

1. Rubber Chemistry & Technology 1939, 556.
2. Rubber Board Bullatin, India, 13.3.1976; 55-57.
3. Small scale rubber Industries, by Goel, 104.
4. RRISL Bulletin Vol.13, 1978 - Commercial manufacture and uses of cyclised rubber.
5. Proceedings of International Rubber Conference 75 Kaulalampour 20 -25 October 1975, Volume IV.
6. Applied Science of Rubber, Nauton, W.J.S.

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ANNEXURE - I

PRODUCTION OF LOW NITROGEN RUBBER:-

The cheapest method of production of low nitrogen rubber is by using papain as the latex coagulant. The following table-1 gives an account of papain concentration and the amount of nitrogen in the coagulated rubber.

Table - 1 Effect of Papain and Dilution on Nitrogen content

D.R.C. % wt.	Papain concentration on rubber % wt.	pH of coagulation	Nitrogen % wt.
30	0	5.2	0.43
30	0.1	6.5	0.3
30	0.2	6.5	0.27
30	0.25	6.5	0.26
30	0.50	6.5	0.26
10	0	5.2	0.41
10	0.25	6.5	0.16

A concentration of papain of 0.25% by wt. on D.R.C. was found to be adequate for obtaining substanilly low nitrogen rubber. Dilution of the D.R.C. from 30% to 10% reduced the nitrogen content from 0.43% to 0.41% in acid coagulation at the same time in papain coagulation there was greater reduction of 0.26% to 0.16%.

The effect of dilution and the presence of a non-ionic stabiliser like Nonidet P-40 on nitrogen content is listed in Table-2.

Table - 2 Effect of Dilution and Concentration of nonidet P-40 on Nitrogen content:

D.R.C.	Nonident P-40 % by wt. on D.R.C.	Nitrogen % by wt. on D.R.C.
35	--	0.31
35	0.25	0.22
35	0.6	0.2
35	0.75	0.14
18	0.25	0.18
18	0.5	0.14
18	0.75	0.11
9	--	0.15
9	0.25	0.13
9	0.5	0.12

The latex was suitably stabilised by nonionic stabliser Nonidet P40, (a 100% active octyl phenolethylene-oxide condensate) The best condition was found to be a dilution of latex with 2-3 volume of water and using papain and Nonidet P-40 at a level of 0.25% w/w on D.R.C.

The use of xylyl mercaptan activates cyclisation reaction as well as reduces the time required for cyclisation. In order to reduce the mastication time and activate cyclisation xylyl mercaptan was added at a level of 5% on D.R.C. as 10% emulsion in water to the field latex before coagulation.

ANNEXURE - A1

Preperation of Low Nitrogen Rubber in Block form:-

The latex stabilised suitably is treated with required amount of papain. The coagulam is washed and fed to hammer mill. The crumbs are dried. The dried crumbs are pressed in the hydraullic press to get the block rubber.

Latex stabilised with Ammonia (0.02%) and
Boric acid (0.2%)
↓
Dilution with two volumes of water.
↓
Addition of 0.25% papain on rubber.
↓
Overnight coagulation and digestion
of proteins.
↓
Creping and washing
↓
Crumbling on the Hammer Mill.
↓
Drying at 100°C for 4½ hours.
↓
Pressed in the hydraullic press into blocks.

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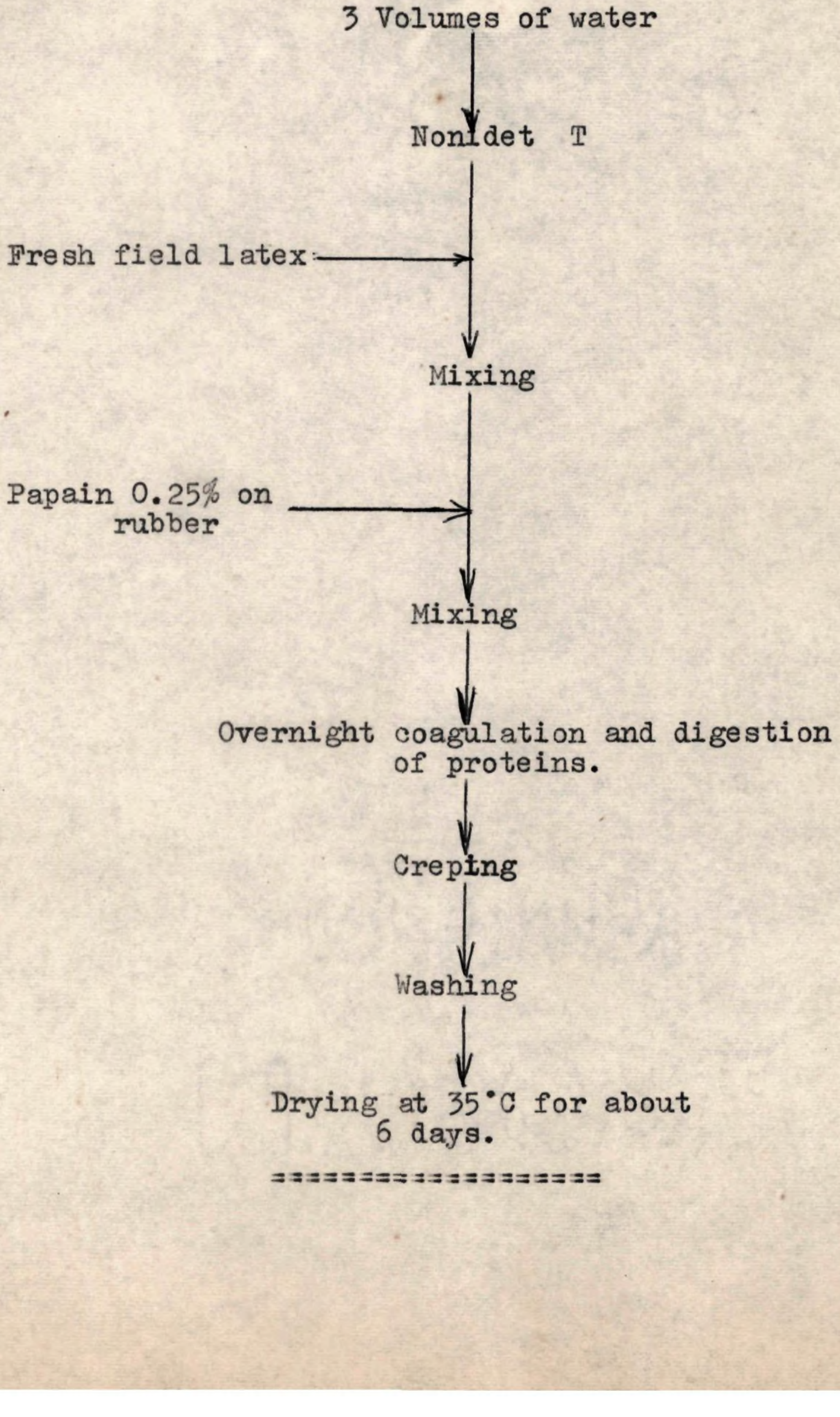
ANNEXURE-A2

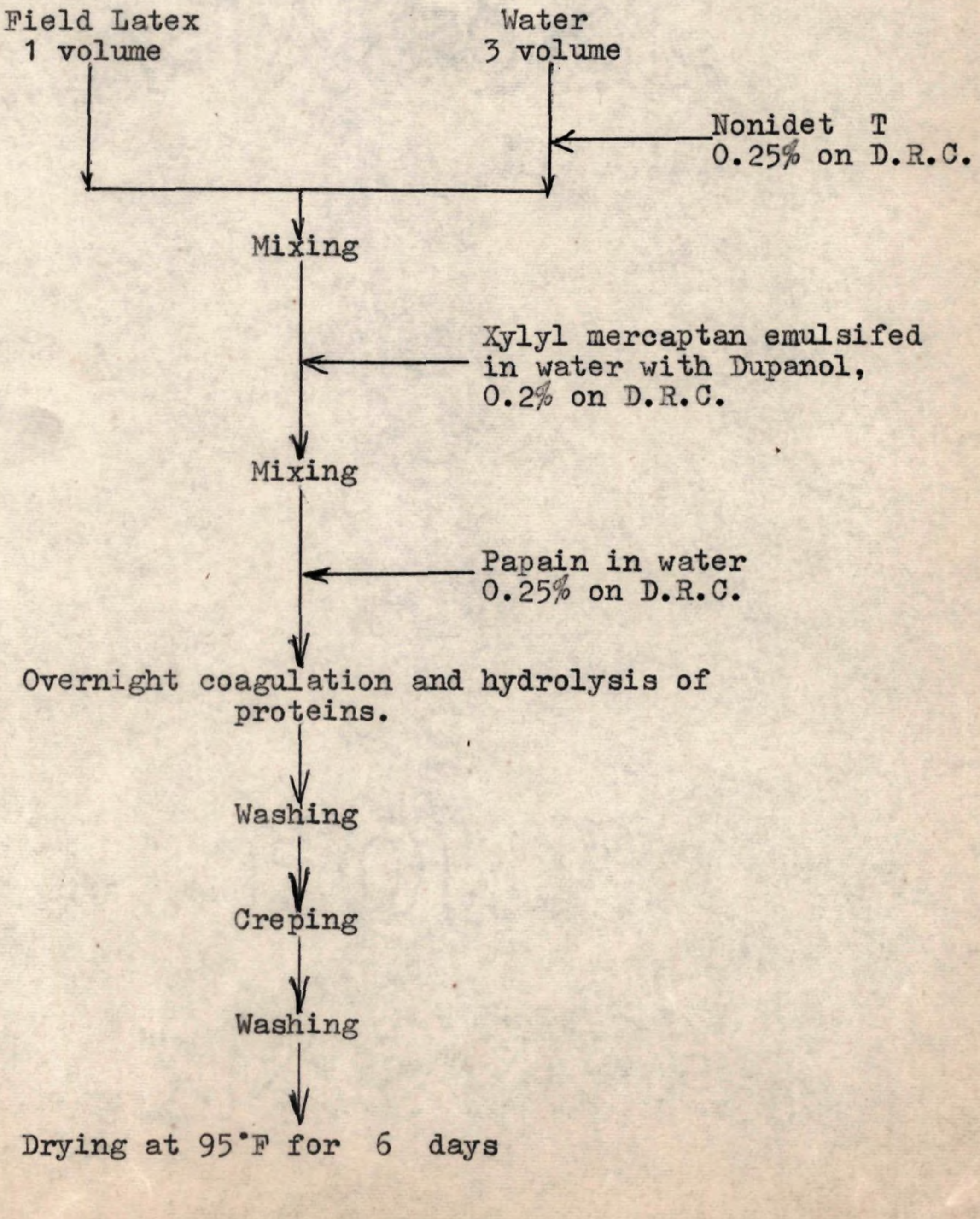
Here the latex is stabilised with Nonidet T and papain is used as the coagulant. The coagulant is washed and fed to the crepe mills and again ~~the product is~~ washed and dried.



ANNEXURE - A3

Preperation of Low Nitrogen Rubber for the manufacture of Cyclised Rubber for Solution applications:-

The field latex is diluted and stabilised with nonionic stabiliser. It is then coagulated with papain after adding xylyl mercaptan as an emulsion into the latex. The coagulam is fe~~e~~d to crepe mill, washed and dried.



ANNEXURE - II

A. COST OF PRODUCTION:

1.	Raw materials (Details table-1)	-	Rs.	6,52,500.00
2.	Salaries & wages (Details table-2)	-	Rs.	51,600.00
3.	Utilities (Details Table - 3)	-	Rs.	5,000.00
4.	Other overheads (Details Table-4)	-	Rs.	39,250.00
5.	Interest on working capital	-	Rs.	14,812.00
6.	Interest on fixed capital	-	Rs.	27,384.00
7.	Depreciation on machinery 10%	-	Rs.	20,700.00
8.	Depreciation on fixed asset and pre-operative cost	-	Rs.	11,450.00
		-	Rs.	8,22,696.00

Annual Production:-

Total production = 155 x 300 = 46,500 kg.

Cost of production/kg. = $\frac{8,22,696}{46,500}$ = 17.70 Rs.

Comparison with HSR:-

Prices of HSR

Type	Basic price Rs.	excise duty Rs.	special excise duty %
1958 B	20.80	2.03	10 of excise duty
1959 A	21.40	2.08	"

From this we can see that cyclised rubber can be produced and marketed at competative prices with HSR.

B. Fixed Capital:-

Machinery (Details in table 5)	- Rs. 2,07,000.00
Other fixed assets (Details in table 6)	- Rs. 5,000.00
Pre operative expense (Details in table 7)	- Rs. 16,200.00
Total	- Rs. 2,28,200.00

The full amount is taken as loan for 12% interest.

The interest is Rs.27,384.00

C. WORKING CAPITAL FOR 3 MONTHS:-

Raw materials	- Rs. 1,38,125.00
Salaries	- Rs. 12,900.00
Utilities	- Rs. 1,250.00
Other overheads	- Rs. 12,312.00
Total	- Rs. 1,64,587.00

75% of this is taken as the loan at 12% interest and the rest is own capital.

Interest for loan - Rs. 14,812.00

Table No. 1

Raw material Requirements:-

150 kg of natural rubber and 15 kg of p-toluene sulphonic acid.

Cost of 1 kg. NR (low nitrogen content)	- Rs.11.5
Cost of total NR for 1 year	- Rs. 5,17,500.00
Cost of p-toluene sulphonic acid for 1 kg.	- Rs. 30/=
Total cost of p-toluene sulphonic acid for 1 year	- Rs. 1,35,000.00
Total raw material cost per annum	- Rs. 6,52,500.00

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Table No. 2

Salaries and Wages:-

Two labourers are engaged in the milling and cyclisation of rubber. Another works on the size reduction machinery. Two more labourers wash and dry the cyclised rubber. The process is supervised by one Supervisor. The office has a Manager, one clerk cum typist and one peon.

Item	No.	Salary/month	Total
Labourer	5	300	18,000.00
Factory Supervisor	1	800	9,600.00
Manager	1	1200	14,400.00
Clerk cum typist	1	500	6,000.00
Peon	1	300	3,600.00
		Total	51,600.00

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Table -No.3

Utilities:-

The total power consumption by the mill and other machinery is taken as 50 KW. Assuming a power factor 0.8, the number of unit required is 63.

Total No. of units/annum = 18,900. ?

Cost/unit = 18 ps.

Total cost/annum = Rs.3,400.00

Water charge @ Rs.1/1000 litre = Rs. 1,600.00

Total = Rs.5,000.00

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Table No. 4

Other overheads:-

Rent for building	-	Rs.	12,000.00
Travelling allowances	-	Rs.	1,000.00
Insurance	-	Rs.	1,500.00
Rent & taxes	-	Rs.	500.00
Selling & distribution @ Rs.0.5/kg.	-	Rs.	22,250.00
Stationary	-	Rs.	1,000.00
Postage, Telephone etc.	-	Rs.	1,000.00
	-	Rs.	39,250.00

Table Mo. 5

Machinery:-

MP	Mixing mill 14″ x 30″	=	Rs. 1,42,000.00
What?	Size reduction machinery-		Rs. 60,000.00
	Aluminum trays		Rs. 5,000.00
	Total		Rs. 2,07,000.00

* * *

Table No. 6

Other Fixed assets:-

Equipment for supplying water	-	Rs. 1,000.00
Fire fighting equipment	-	Rs. 500.00
Furniture	-	Rs. 3,000.00
Tools and equipments	-	Rs. 500.00
Total	-	Rs. 5,000.00

* * *

Table No. 7

Pre-operative expenses:-

Interest on fixed capital at 12% for 6 months.	-	Rs. 13,200.00
Establishment	-	Rs. 2,000.00
Travelling expenses	-	Rs. 500.00
Legal charges	-	Rs. 500.00
Total	-	Rs. 16,200.00

* * *

D. CAPITAL RAISING:-

Fixed Capital	- Rs. 2,28,200.00
Working capital	- Rs. 1,64590 .00
	Rs. 3,92,790.00

The full amount of fixed capital is obtained from any financial institutions like K.F.C. at 12 % interest. 75% of the working capital from any nationalised banks. The rest is own capital.

Loan from any financial institutions	- Rs. 2,28,200.00
Loan from any nationalised bank	- Rs. 1,23,442.00
Own capital	- Rs. 41,148.00

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