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# MASTICATION AND COMPOUNDING OF NATURAL RUBBER IN AN OXYGEN-FREE ATMOSPHERE

by

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# Mastication and Compounding of Natural Rubber in an Oxygen-free Atmosphere

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SUMMARY.—Confirmation has been obtained that raw rubber when masticated in the absence of oxygen undergoes only a limited amount of breakdown; and it has been shown that two of the better known so-called "peptisers" or chemical plasticisers of rubber, viz. mercaptobenzthiazole and *o-o'*-dibenzamidodiphenyl disulphide, require oxygen to be effective.

A range of pure gum rubbers has been compounded under nitrogen, and the physical properties after vulcanisation compared with corresponding air-compounded rubbers. Some types of acceleration give vulcanisates whose physical properties are very sensitive to changes in the viscosity of the unvulcanised stock, decrease in viscosity giving decreased modulus. Other types of acceleration, notably "boosted" combinations which give high modulus vulcanisation, are insensitive to stock viscosity changes over a wide range.

## I. MASTICATION AND THE EFFECT OF PLASTICISERS

### INTRODUCTION

The important role played by oxygen in the breakdown of rubber during mastication has been established by Cotton and Busse.[1,2] However, the effect of plasticisers and in particular chemical plasticisers, often incorrectly termed "peptisers," in the absence of oxygen has received only slight attention.[3,4,5]

This subject and the closely related question of the production of vulcanisable compounds in an inert atmosphere appeared to need a fuller investigation; and in this paper are recorded some results and observations obtained from experiments conducted in an atmosphere of nitrogen.

The first part of the paper deals with the relative effect of the mastication of natural rubber in air and in nitrogen over a temperature range from 50° to 140° C.; together with a brief survey of the effect of common plasticisers and softeners and a more detailed treatment of two chemical plasticisers, mercaptobenzthiazole and *o-o'*-dibenzamidodiphenyl disulphide.

The second part covers the production of a number of pure gum compositions under nitrogen and comparison of the physical properties of the resulting vulcanisates with those of similar compounds obtained by normal air compounding.

### EXPERIMENTAL

*Apparatus.*—The apparatus employed was a small laboratory-type Size B Bridge Banbury internal mixer with a capacity of about 500 g. of raw rubber. The machine was suitably modified for operating under nitrogen by fitting a metal top plate with inlet and outlet nipples, and by sealing all other outlets, e.g. chamber seams, etc., with asbestos putty. Efficient sealing of the floating bearings employed on this type of machine could not be achieved, and it was therefore decided to operate with a small excess pressure of nitrogen inside the chamber, equivalent to 1 in. of water. This excess pressure was recorded by means of a water manometer connected to the outlet nipple, and although some fluctuation occurred during operation caused by changes in bearing clearance, the pressure never dropped below ½ in. of water, and a fairly constant mean pressure could be maintained. Since complete displacement of air by nitrogen would be very unlikely under these conditions, no attempt was made to degas the rubber prior to mastication and oxygen-free grade cylinder nitrogen (less than 10 volumes of oxygen per million volumes) was used, without further purification. A plunger bar was attached to the top plate to prevent the charge from riding off the rotors during mastication, and as it was necessary to introduce a full charge and clamp the machine down before setting it in motion, a batch weight of 200 g. of rubber was used throughout the mastication experiments to avoid stalling the motor when operating from the cold.

*Determination of degree of breakdown.*—Degree of breakdown was measured on a standard Mooney viscometer, operating at a temperature of 100° C. with a disc rotor (1½ in. diameter) revolving at a speed of 2 revolutions per minute. The samples were allowed to stand in air for 24 hours after mastication, before being tested. The values recorded are dial readings after 1 minute warming up and 3 minutes running.

*Reproducibility of results.*—A preliminary set of experiments was carried out to determine the reproducibility of results and the period of sweep out with nitrogen needed to ensure removal of air from the apparatus before commencing mastication (see Table 1). A 10-minute period of sweep out was established as satisfactory and was used in all subsequent mastication experiments under nitrogen.

TABLE 1

REPRODUCIBILITY OF RESULTS

20 minutes' Mastication

| Atmosphere | Time of sweep out (mins.) | Mooney viscometer readings | | |
|---|---|---|---|---|
| Air | | 40·5 | 42·0 | 42·0 |
| Nitrogen | 5 | | 103·5 | |
| | 10 | | 102·5 | |
| | 15 | | 102·5 | |

*Mastication of smoked sheet.*—Mastication was carried out in air and in nitrogen: (*a*) with cold water flowing through the casing and rotor, (*b*) with open steam through the casing and rotor, and (*c*) with steam at 40 lb. per sq. in. through the casing and rotor.

With cold mastication an approximate estimate of the temperature reached by the rubber during working was obtained by embedding a needle pyrometer in the centre of the mass immediately on removal from the mixer. Temperature readings between 43° and 58° C. were observed, nitrogen mastication giving in every case higher values than air mastication, the mean difference being 5° C.

The results of mastication in air and in nitrogen are shown in Fig. 1. Experiments in the cold and at 100° C. were carried out with a sample of smoked sheet rubber with an initial Mooney viscosity of 97 to 98.

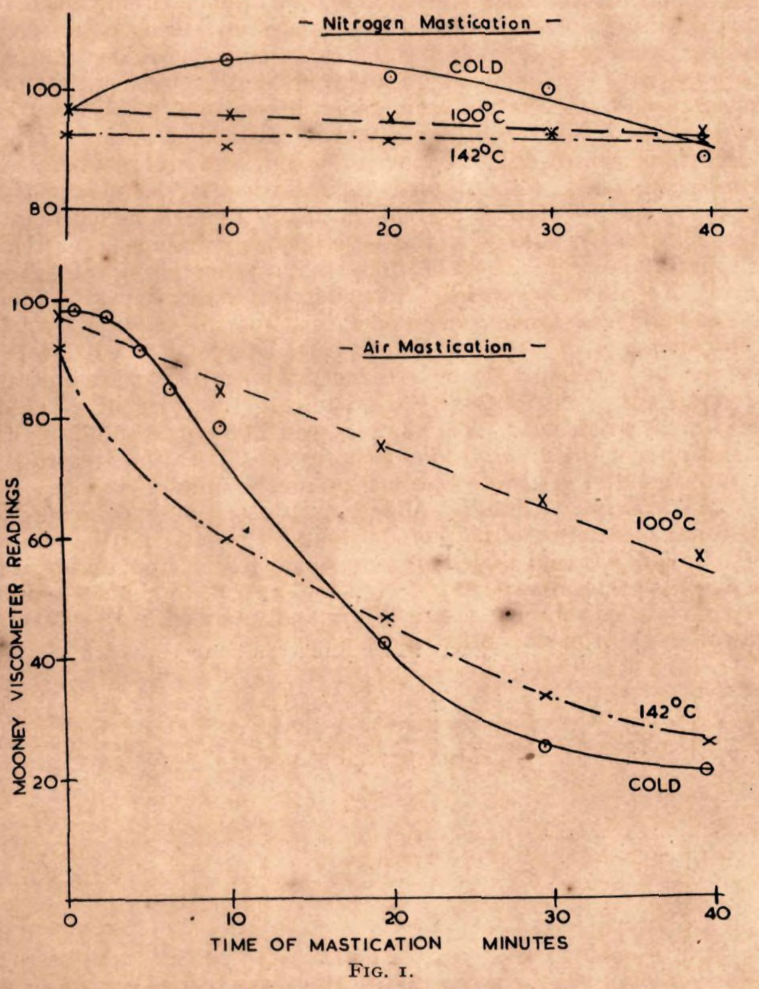


FIG. 1.

Mastication of Smoked Sheet.

The work at 142° C. was with smoked sheet rubber with an initial Mooney viscosity of 92.

The results obtained in air are consistent with the well-established practice of cold mastication for maximum breakdown and mastication at about 100° C. for minimum breakdown.

The very slight breakdown under nitrogen at 100° and 142° C. suggests that breakdown in air is entirely oxidative, but the initial increase in viscosity followed by breakdown as recorded at 50° C. means that the possibility of some other parallel mechanism such as mechanical breakdown cannot be ruled out. A further investigation of the effect of mastication in the cold under nitrogen was therefore carried out over a longer period using a fresh sample of No. 1x ribbed smoked sheet rubber with a Mooney viscosity of 100; and also a batch of U.S.F.[6] rubber of Mooney viscosity 87.

The results on the three rubbers are shown in Fig. 2. None gives any indication of immediate breakdown, but the well-marked initial increase in viscosity shown by the first sample of smoked sheet and by the U.S.F. rubber appears to be absent in the case of the second smoked sheet sample.

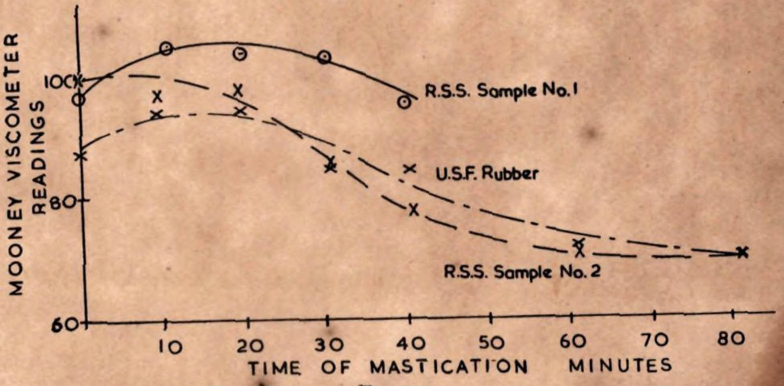


FIG. 2.

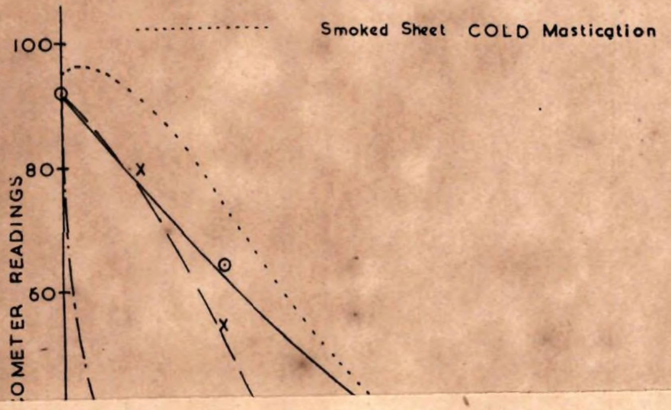
Cold Mastication of Raw Rubber in Nitrogen.

*Mastication of smoked sheet rubber in the presence of the so-called "peptisers."*—During the past decade many chemicals have appeared which have the property of accelerating the breakdown of raw rubber during mastication, particularly at temperatures of the order of 120° to 140° C. These are in many instances referred to as "peptisers," a term which suggests a physical or mechanical action. Some evidence has already been advanced to suggest that these compounds require oxygen to be effective,[4] and a detailed study of their action under nitrogen appeared a likely method of obtaining further information on their plasticising properties. Series of experiments similar to those carried out with raw rubber were conducted using two of the best known of these peptisers.

(*a*) *Mercaptobenzthiazole.*—One part by weight of commercial mercaptobenzthiazole per hundred parts by weight of rubber was added to the batch in the Banbury before mastication was commenced.

In the cases of mastication under nitrogen at 100° and 142° C., where mercaptobenzthiazole was found to be ineffective, very considerable oxidation of the rubber took place if the batch was allowed to cool down in air after removal from the mixer. This was shown in the development of a syrupy, very sticky film over the surface of the rubber mass and reproducible Mooney viscosity figures could not be obtained. It was possible to prevent this by cooling down each batch under nitrogen in the mixer, but it was found that removal from the mixer while hot, followed by immediate submersion in cold water, proved just as effective in preventing oxidation, and this method was adopted. This effect made it impossible to obtain batch temperatures for hot mastication.

The results, which are plotted in Figs. 3 and 4, indicate that in air the main effect of mercaptobenzthiazole is of a chemical nature, there being a marked increase in rate of breakdown with increase in temperature. The absence of further breakdown after an initial drop of some 8 to 10 Mooney points, when working under nitrogen at 100° and 142° C., gives confirmation of this view and shows that the process is a chemical plasticisation requiring oxygen. The alternative explanation, that mechanical lubrication of the rubber molecules is occurring, seems unlikely, in view of this absence of continued breakdown at 100° and 142° C., and was refuted by acetone extraction of the rubbers from the mastication experiments. The results of these are shown in Table 2,



Errata: The diagrams appearing above Figures 3 ar
on pages 313 and 315 should be transpos

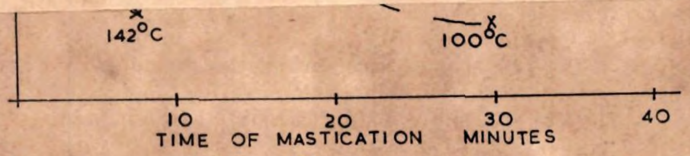


FIG. 3.

Mastication of Smoked Sheet and Mercaptobenzthiazole in air.

acetone extraction being carried out under nitrogen for a period of 24 hours. The increase in viscosity of a normally masticated rubber is due to the removal of the natural resins and fatty acids. As the increase was not significantly greater in the case of the rubbers containing mercaptobenzthiazole, any lubrication effect must be small.

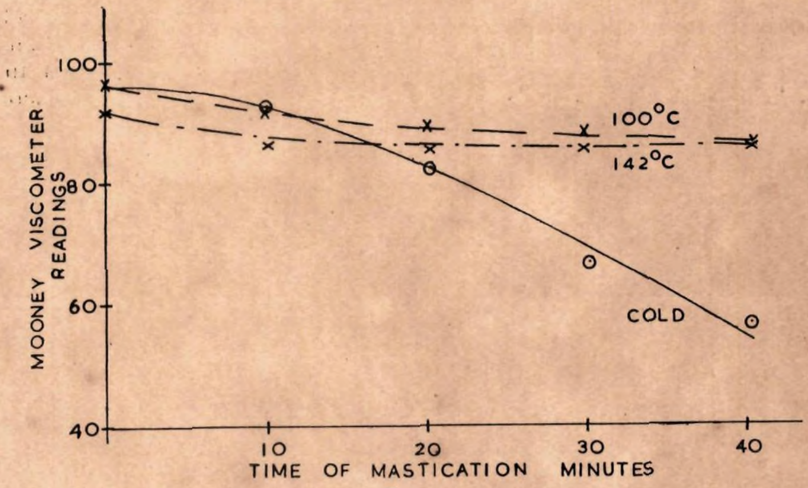


FIG. 4.

Mastication of Smoked Sheet and Mercaptobenzthiazole in Nitrogen.

TABLE 2

ACETONE EXTRACTION OF MASTICATED RUBBER

| Composition | Time of mastication (min.) | Temp. | Atmosphere | Mooney viscometer reading | | |
|---|---|---|---|---|---|---|
| | | | | Before extraction | After extraction | Increase |
| Smoked sheet rubber .. | 10 | 100° C. | Air | 89·5 | 95·0 | 5·5 |
| Smoked sheet rubber + 1 part of mercaptobenzthiazole .. .. .. | 10 | 100° C. | Air | 38·0 | 45·0 | 7·0 |
| Smoked sheet rubber + 1 part of mercaptobenzthiazole .. .. .. | 40 | Cold | Nitrogen | 56·0 | 63·0 | 7·0 |

The breakdown recorded in the cold under nitrogen appears anomalous. It was confirmed by a number of independent observations, and did not take place if an inert filler, such as clay, was substituted for the mercaptobenzthiazole, i.e. it could not be attributed to oxygen carried in by the added powder. As will be shown later, a similar effect was obtained with *o-o'*-dibenzamidodiphenyl disulphide, and this phenomenon will be considered further in the general discussion of the mastication data.

(*b*) *o-o′-Dibenzamidodiphenyl disulphide*.—The recent appearance on the commercial market of *o-o′*-dibenzamidodiphenyl disulphide allowed the comparison of its properties with those of mercaptobenzthiazole to be made. A series of experiments similar to the above was carried out using 1 part by weight of *o-o′*-dibenzamidodiphenyl disulphide per 100 parts by weight of rubber. As with mercaptobenzthiazole, it was found necessary to cool down under water, after mastication under nitrogen at 100° and 142° C., to prevent surface oxidation. The results are plotted in Figs. 5 and 6.

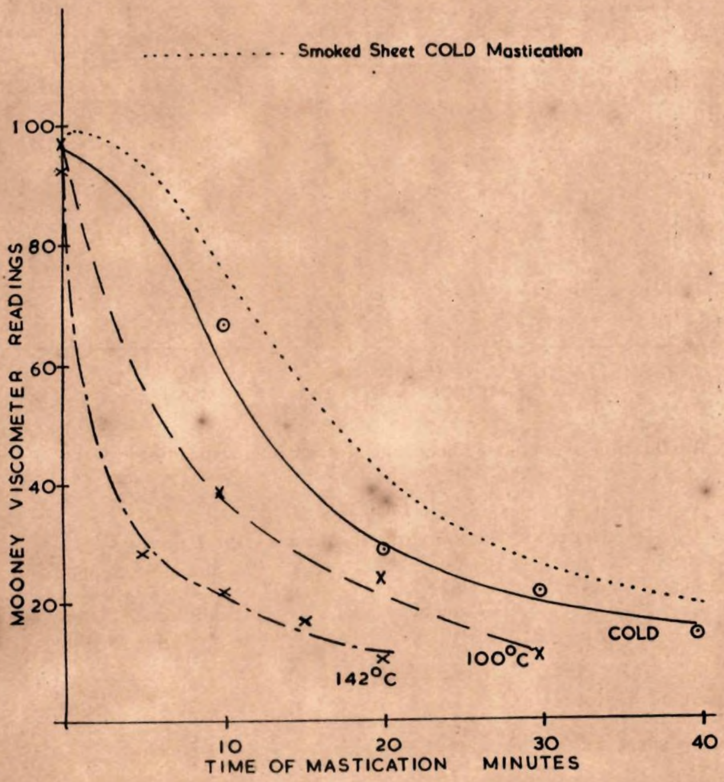


FIG. 5.

Mastication of Smoked Sheet and *o-o′*-dibenzamidodiphenyl disulphide in air.

The general effect of *o-o′*-dibenzamidodiphenyl disulphide is similar to that of mercaptobenzthiazole. In air, below 100° C., it is a little less efficient, and above 100° C. more efficient than a corresponding amount of mercaptobenzthiazole. Its similarity under nitrogen is also very marked: only a slight breakdown at 100° and 142° C., but considerable breakdown in the cold; and it is evident that the mode of operation of these two compounds in assisting the breakdown of raw rubber is the same.

It was of interest to examine their relative effects as chemical plasticisers in air at concentrations below 1 part per 100 parts of rubber. Comparative data for air mastication for 5 minutes at 142° C. is plotted in Fig. 7. Efficiency of breakdown increases with increasing amounts of the plasticiser and below 0·5 parts per 100 parts of rubber there is no significant difference between them. However, it is claimed that *o-o′*-dibenzamidodiphenyl disulphide has only slight effect on the cure, whereas mercaptobenzthiazole, being in addition an accelerator of vulcanisation, must be allowed for in subsequent compounding.

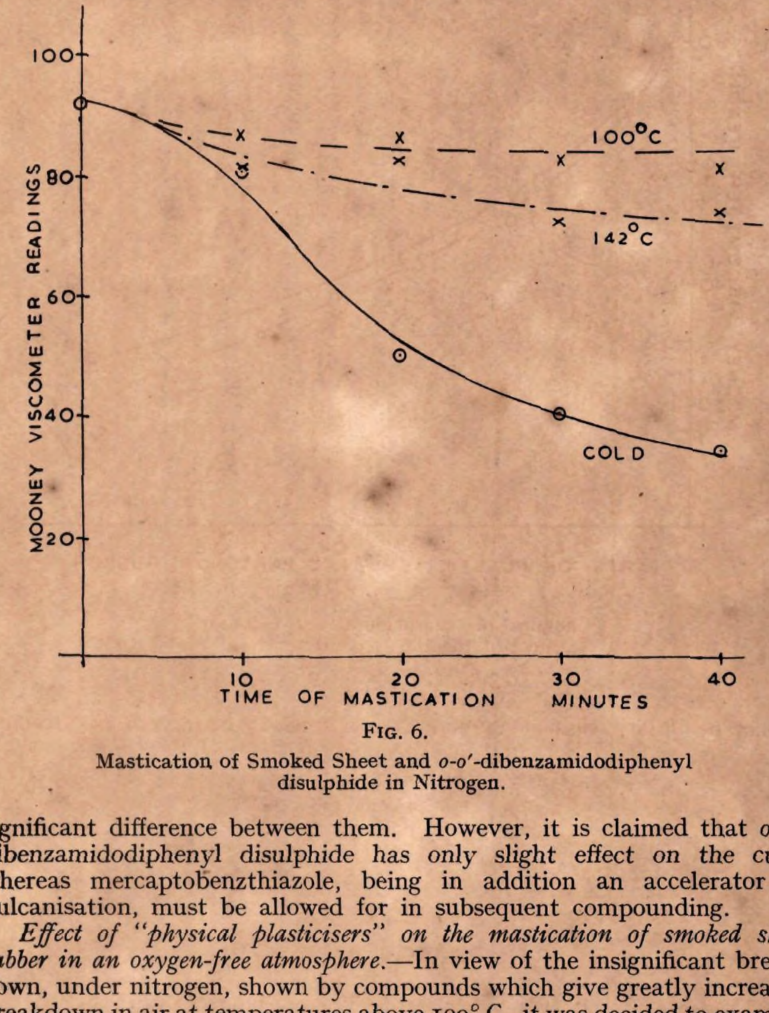


FIG. 6.

Mastication of Smoked Sheet and *o-o′*-dibenzamidodiphenyl disulphide in Nitrogen.

*Effect of "physical plasticisers" on the mastication of smoked sheet rubber in an oxygen-free atmosphere.*—In view of the insignificant breakdown, under nitrogen, shown by compounds which give greatly increased breakdown in air at temperatures above 100° C., it was decided to examine the behaviour of some of the more common commercial plasticisers when masticated with rubber in the absence of air. Comparisons were made for a 20 minutes' period of mastication under nitrogen at a mixer-temperature of 100° C., with 3 parts by weight of the compound per

100 parts by weight of rubber, added before mastication was commenced. The resulting Mooney viscosity values are recorded in Table 3, the rubber used being No. 1x ribbed smoked sheet rubber with a Mooney value of 97 to 98. The small decreases in viscosity are attributed to varying degrees of internal lubrication, being most marked in the case of fatty

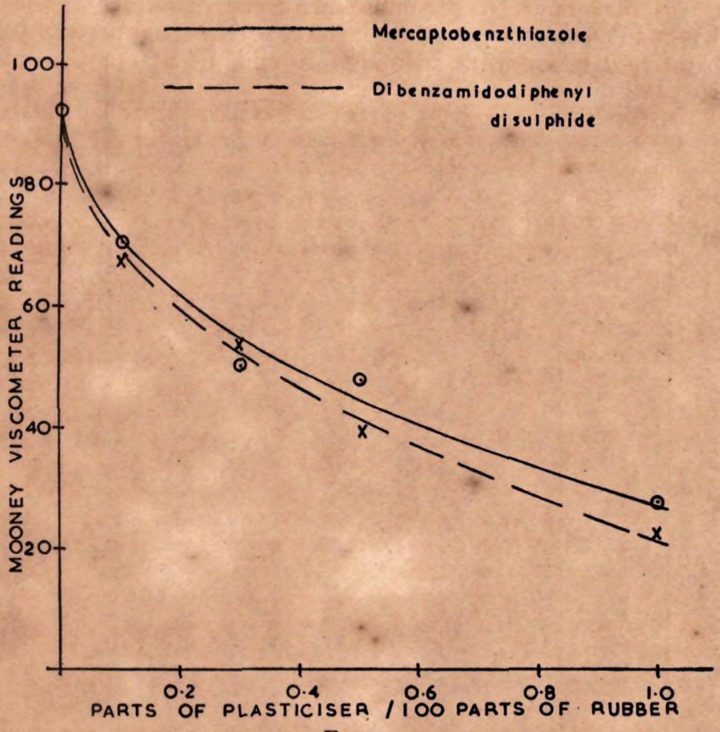


FIG. 7.

Chemical plasticisation at 142° C. in air.
Effect of plasticiser concentration.

TABLE 3

EFFECT OF PLASTICISERS ON SMOKED SHEET RUBBER MASTICATED IN NITROGEN

Mooney Viscosity of Original Sheet 97 to 98

| Plasticiser | Mooney viscometer readings | Plasticiser | Mooney viscometer readings |
|---|---|---|---|
| Stearic acid . . . . . . | 85·5 | Pine oil | 94·0 |
| Zinc laurate . . . . . . | 83·0 | | |
| Mineral oil . . . . . . | 90·0 | *Plastogen | 91·0 |
| tri-Cresyl phosphate . . . . | 93·0 | †Bondogen | 91·0 |
| di-Butyl phthalate . . . . | 91·0 | | |
| Rosin oil . . . . . . | 92·0 | | |

* Plastogen—1·6 per cent. sulphonated petroleum product in mineral oil.
† Bondogen—75 per cent. sulphonated petroleum product in butyl alcohol.

acid types. The greater lubricating effect of fatty acids and their zinc salts as compared with similar additions of hydrocarbon oils has been commented on by previous workers in this field.[3,4] The fact that this effect is also observed in nitrogen means that a chemical reaction as tentatively suggested by Busse and Cunningham is unlikely.

### DISCUSSION OF MASTICATION DATA

Further confirmation has been obtained of Cotton's and Busse's findings on the importance of oxygen for the breakdown of raw rubber during normal mastication. The results for mastication in the presence of mercaptobenzthiazole and *o-o'*-dibenzamidodiphenyl disulphide show that here too oxygen plays a prominent part, and the lack of continued breakdown when working under nitrogen, as compared with a marked increase over normal breakdown when working in air, indicates that the peptising action of these compounds is due to their ability to increase the rate or efficiency of oxidative breakdown of the rubber molecule. In fact, the term "chemical plasticiser" in contradistinction to "physical plasticiser" referred to in Table 3, should be used in place of "peptiser."

At the moment no really satisfactory explanation can be brought forward to account for the breakdown which takes place under nitrogen in the cold in the presence of these compounds. It may be pointed out that in nitrogen the breakdown with or without chemical plasticisers is insignificant at 100° and 142° C., but exists to a greater or lesser extent in the cold. These latter effects suggest that trapped air may not escape at the lower temperature and is sufficient to produce breakdown which is greater in efficiency in the presence of an oxidative catalyst even at temperatures around 50° C.

Mastication of smoked sheet rubber under nitrogen at 100° C. where no breakdown took place and any trapped air should have been displaced, followed by cooling, addition of mercaptobenzthiazole, and continued mastication in the cold under nitrogen, was carried out in an attempt to substantiate this theory. However, breakdown was obtained of the same order as observed by direct cold mastication of smoked sheet rubber with mercaptobenzthiazole under nitrogen.

At this stage the results and observations recorded above do not provide any definite answer to the question as to whether breakdown of rubber during mastication is a mechanical as well as an oxidative process. Although most of the evidence points to the latter, and establishes its role in the presence of chemical plasticiser, the greater breakdown in the cold than at 100° C. during normal air mastication, and the breakdown observed in the cold under nitrogen in the presence of mercaptobenzthiazole and *o-o'*-dibenzamidodiphenyl disulphide, suggest some parallel mechanism of a different character.

## II. PROPERTIES OF PURE GUM VULCANISATES COMPOUNDED IN AN OXYGEN-FREE ATMOSPHERE

### INTRODUCTION

The observation of the almost complete lack of breakdown of raw rubber when masticating under nitrogen, as recorded in the first part of this paper, suggested the possibility of producing vulcanisable materials without appreciably reducing the molecular weight of the rubber employed. Comparison of the physical properties of the resulting vulcanisates with those of normal air-compounded materials would then provide information on variations of physical properties with stock viscosity in a range not previously investigated.

## EXPERIMENTAL

During the development of a technique for the production of compounded stocks under nitrogen, where only slight breakdown of the rubber takes place it was observed that (*a*) complete compounding in the cold was not successful as the lack of breakdown, and the absence of any marked thermal softening, resulted in a poor dispersion of the vulcanising ingredients, and (*b*) compounding at 100° C. often resulted in considerable scorching of the stock even with low sulphur and a delayed action type of acceleration.

The method finally adopted was to add all the compounding ingredients with the exception of the sulphur and to masticate at 100° C. under nitrogen for 10 minutes. The machine was then stopped and cold water circulated through the blades and rotor for 5 minutes during which time the sulphur was added through an opening in the top plate. After sweeping out again with nitrogen, mastication was continued for a further 5 minutes, the temperature of the stock being controlled by use of water or steam as desired, to ensure dispersion of the sulphur without any pre-vulcanisation of the compound.

With many of the nitrogen-compounded stocks it was found that in attempting to produce a smooth press-cured sheet for physical testing, considerable curing occurred before sufficient flow had taken place to fill the mould. The resulting sample showed marked shrinkage on removal from the mould, had an uneven surface, and was of little value for testing purposes. The effect was overcome almost entirely by pressing out the compounded rubber under a cold press to as thin a sheet as possible, immediately on removal from the mixer, and allowing it to cool down in that condition. Shrinkage took place on removal from the press, but flat sections could be cut for moulding purposes. These showed only very slight contraction after vulcanisation, had a good smooth surface, and gave reproducible results in testing. All samples were press cured at 142° C. (40 lb. per sq. in. steam pressure) to produce test sheets 6 in. × 6 in. × $\frac{1}{8}$ in.

## COMPOUND DATA AND RESULTS

*Cold breakdown in air and in nitrogen.*—In view of the breakdown observed during mastication under nitrogen in the cold in the presence of mercaptobenzthiazole, it was decided to compare the physical properties after vulcanisation of two identical pure gum compounds, one with breakdown of the rubber as above, and one with normal cold breakdown in air, to give a similar stock plasticity in each case. For nitrogen compounding, the rubber was masticated in the cold under nitrogen with the mercaptobenzthiazole for 30 minutes, the remainder of the compounding ingredients added, and a further 10 minutes' period of mastication under nitrogen allowed for dispersion. For air-compounding, the rubber with the mercaptobenzthiazole was masticated in air for 7 minutes in the cold, and after adding the compounding ingredients, masticated under nitrogen for a further 10 minutes. Compound formulation and physical test results are given in Table 4, from which it is evident that the physical properties of the resulting vulcanisates are very similar.

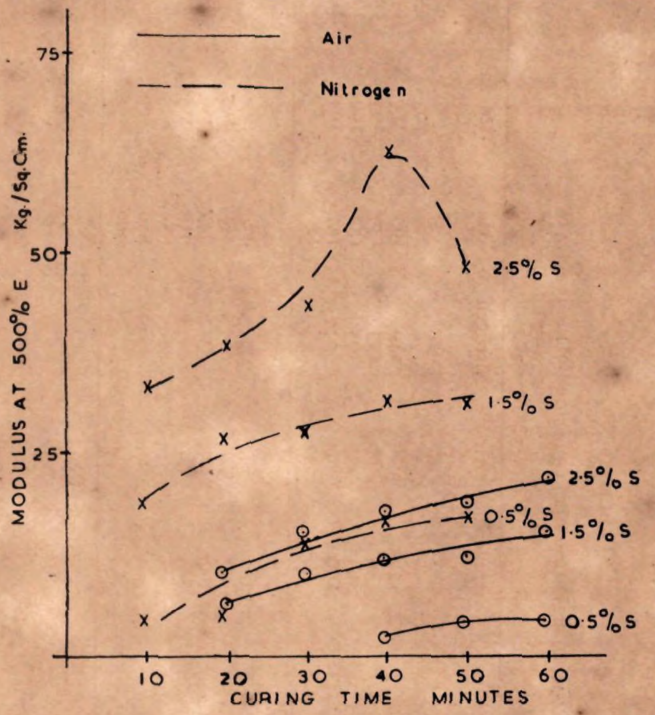


FIG. 8.

Benzthiazyl disulphide acceleration.

TABLE 4

COLD MASTICATION OF SMOKED SHEET RUBBER + MERCAPTOBENZTHIAZOLE IN AIR AND IN NITROGEN. PHYSICAL PROPERTIES OF VULCANISATES

| Composition | | Atmosphere | Mooney viscometer reading | Time of cure at 142° C. (min.) | Tensile strength (kg. per sq. cm.) | Elongation at break % | Modulus at 500% E. (kg. per sq. cm.) |
|---|---|---|---|---|---|---|---|
| Smoked sheet rubber | 100 | | | | | | |
| Zinc oxide .. .. | 5 | Air | 73 | 10 | 232 | 830 | 32 |
| Sulphur .. .. | 3 | | | 20 | 222 | 810 | 35 |
| Stearic acid .. .. | 1 | | | 30 | 235 | 835 | 35 |
| Mercaptobenzthiazole | 1 | | | | | | |
| | | Nitrogen | 70 | 10 | 219 | 790 | 35 |
| | | | | 20 | 239 | 825 | 31 |
| | | | | 30 | 218 | 815 | 29 |

### TABLE 5

BENZTHIAZYL DISULPHIDE ACCELERATION. TENSILE DATA

| Compound . . . . | A | | B | | C | | D | | E | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen |
| *Tensile strength* (kg. per sq. cm) | | | | | | | | | | |
| 10 min. at 142° C. | — | 9 | — | 52 | — | 75 | — | 107 | — | 138 |
| 20 " " | — | 14 | 27 | 122 | 80 | 140 | 105 | 174 | 117 | 171 |
| 30 " " | — | 87 | 63 | 156 | 106 | 173 | 139 | 194 | 122 | 180 |
| 40 " " | 10 | 103 | 71 | 163 | 133 | 165 | 152 | 190 | 165 | 165 |
| 50 " " | 15 | 121 | 98 | 166 | 95 | 204 | 137 | 194 | 188 | 162 |
| 60 " " | 26 | | 104 | | 141 | | 186 | | 200 | |
| *Elongation at break* (per cent.) | | | | | | | | | | |
| 10 min. at 142° C. | — | 648 | — | 755 | — | 807 | — | 815 | — | 815 |
| 20 " " | — | 723 | 940 | 857 | 955 | 855 | 945 | 840 | 930 | 790 |
| 30 " " | — | 885 | 960 | 863 | 905 | 867 | 910 | 835 | 840 | 775 |
| 40 " " | 760 | 868 | 910 | 870 | 915 | 820 | 885 | 815 | 878 | 705 |
| 50 " " | 775 | 876 | 925 | 865 | 870 | 865 | 870 | 800 | 888 | 710 |
| 60 " " | 860 | | 900 | | 896 | | 900 | | 870 | |
| Mooney viscosity of compounded stock | 45 | 89 | 50 | 92 | 49·5 | 89 | 53 | 92·5 | 49·5 | 95 |

*Benzothiazyl disulphide acceleration.*—A series of compounds covering a range of sulphur contents was prepared under nitrogen by the method already detailed; and a similar series for comparison by air mastication in the mixer at 100° C. for 5 minutes with all the compounding ingredients except the sulphur, followed by cooling and addition of sulphur and a further 5 minutes' mastication to bring the stock viscosity into the region of 50 Mooney. Details of the compositions are as follows:—

*Base composition.*

| | |
|---|---|
| Smoked sheet rubber | 100 |
| Zinc oxide .. | 5 |
| Stearic acid .. | 1 |
| Benzthiazyl disulphide | 0·5 |

| Compound | A | B | C | D | E |
|---|---|---|---|---|---|
| Parts of sulphur per 100 parts of rubber .. | 0·5 | 1·0 | 1·5 | 2·0 | 2·5 |

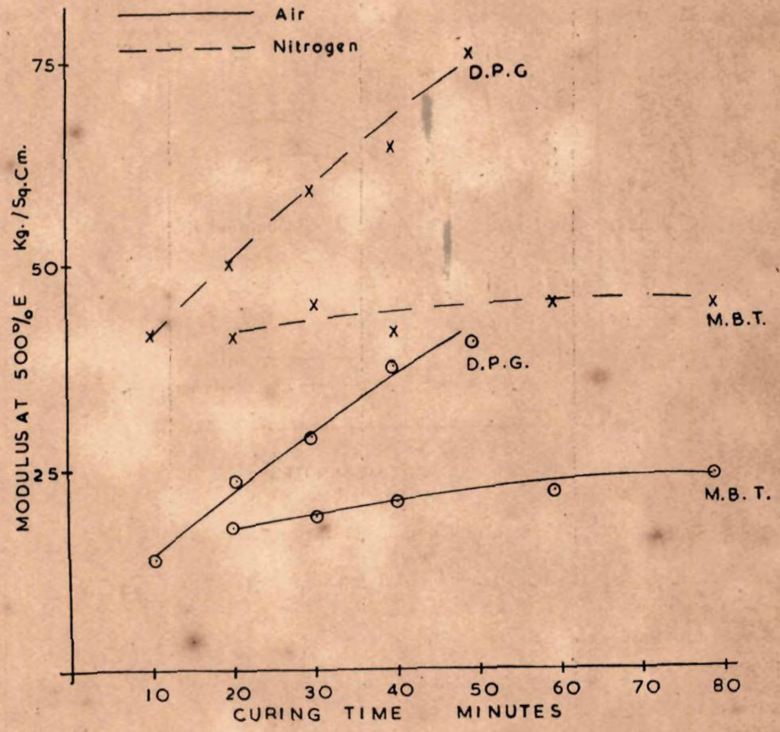


FIG. 9.

Mercaptobenzthiazole and Diphenylguanidine acceleration.

Comparison of these compounds by plotting the modulus at 500 per cent. elongation against the time of cure is shown in Fig. 8. The increase in modulus obtained by reducing the breakdown is maintained over the range from low to normal sulphur content. The data given in Table 5 show that even with an abnormally low sulphur and low acceleration, an appreciable tensile strength is realised. The differences in the values at the shorter cure times are of considerable interest.

*Normal and "boosted" acceleration.*—A number of pure gum compounds were examined covering a range from very low to very high modulus type acceleration. N-cyclohexyl-2-benzothiazole sulphenamide was used as a basis for all the boosted accelerator combinations, as it was found

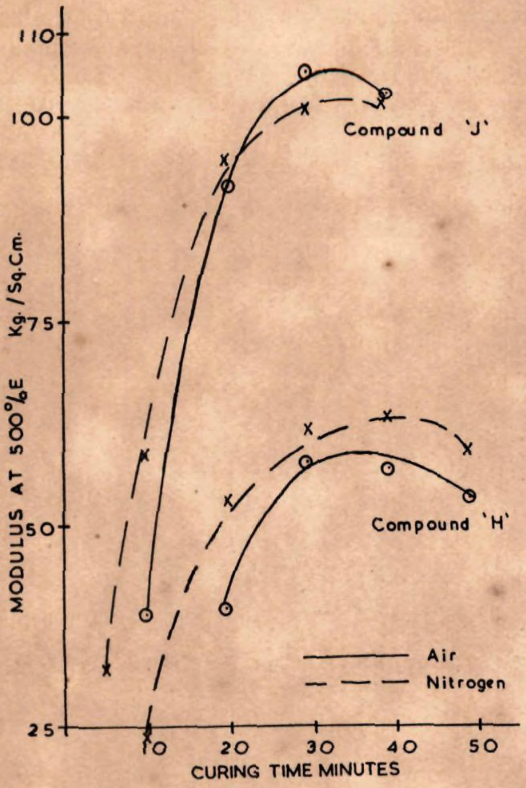


FIG. 10.

High modulus acceleration.

TABLE 6

PURE GUM COMPOSITIONS

| Compound | F | G | H | J | K | L |
|---|---|---|---|---|---|---|
| Smoked sheet rubber .. | 100 | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide .. .. .. | 5 | 5 | 5 | 5 | 5 | 5 |
| Stearic acid .. .. | 0·5 | 1 | 1 | 1 | 1 | 1 |
| Sulphur .. .. .. | 3·5 | 3·25 | 3 | 3 | 3 | 3 |
| Mercaptobenzthiazole .. | 0·5 | — | — | — | — | — |
| Diphenylguanidine .. | — | 1·25 | — | 0·5 | — | — |
| N-Cyclohexyl-2-benzthiazole sulphenamide .. | — | — | 0·5 | 0·5 | 0·5 | 0·5 |
| Tetramethylthiuram disulphide .. .. | — | — | — | — | 0·1 | 0·2 |

that its delayed action effect was sufficient to allow safety in processing and good results in moulding. Compositions are shown in Table 6. Plots of modulus at 500 per cent. elongation against time of cure are shown in Figs. 9, 10, and 11. With mercaptobenzthiazole and diphenyl quanidine acceleration a considerable increase in modulus is produced by preventing breakdown of the compounded stock; but with the boosted high modulus types this increase is no longer apparent. The data in Table 7 is of interest in showing the difference in tensile strength given by air and nitrogen compounding.

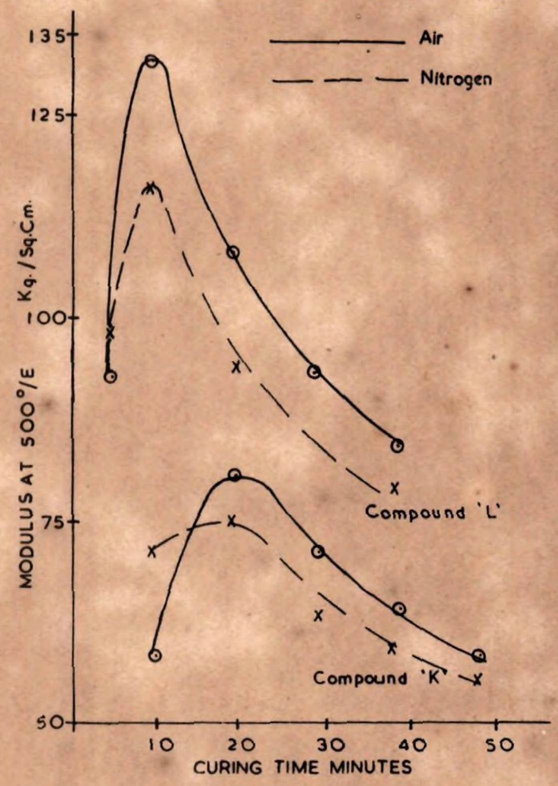


FIG. 11.
High modulus acceleration.

*Tetramethyl thiuram disulphide vulcanisation.*—A pure gum compound vulcanised with tetramethyl thiuram disulphide was similarly investigated; the composition and physical data obtained are given in Table 8 and the modulus at 500 per cent. elongation is plotted against time of cure in Fig. 12. Here again nitrogen-compounding gives greatly increased modulus and the full tensile strength is developed in a shorter time of cure.

## TABLE 8

TETRAMETHYLTHIURAM DISULPHIDE VULCANISATION
COMPOSITION AND PHYSICAL TEST DATA

| Composition | | Atmosphere | Mooney viscometer reading | Time of cure at 142° C. (min.) | Tensile *strength* (kg. per sq. cm.) | Elonga*tion at* break % |
|---|---|---|---|---|---|---|
| Smoked sheet rubber | 100 | | | 10 | 142 | 883 |
| Zinc oxide .. .. | 2 | Air | 48·5 | 20 | 162 | 817 |
| Tetramethylthiuram disulphide .. | 3 | | | 30 | 175 | 793 |
| | | | | 40 | 179 | 775 |
| | | | | 50 | 201 | 783 |
| | | Nitrogen | 92 | 10 | 206 | 793 |
| | | | | 20 | 248 | 777 |
| | | | | 30 | 246 | 760 |
| | | | | 40 | 257 | 742 |
| | | | | 50 | 239 | 727 |

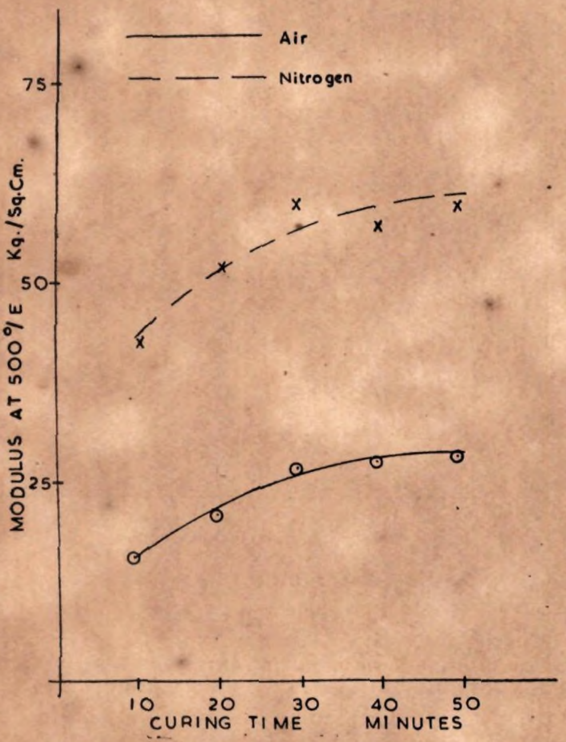


FIG. 12.

Tetramethylthiuram disulphide vulcanisation.

TABLE 7

PURE GUM COMPOSITIONS. TENSILE DATA

| Compound .. .. | F | | G | | H | | J | | K | | L | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen | Air | Nitrogen |
| *Tensile strength* (kg. per sq. cm.) | | | | | | | | | | | | |
| 5 min. at 142°C. | — | — | — | — | — | — | 134 | 222 | — | — | 209 | 267 |
| 10 " " | — | — | 130 | 188 | — | 196 | 304 | 313 | 296 | 332 | 262 | 274 |
| 20 " " | 145 | 201 | 199 | 233 | 318 | 323 | 308 | 297 | 266 | 306 | 194 | 245 |
| 30 " " | 171 | 221 | 228 | 256 | 311 | 313 | 281 | 293 | 247 | 284 | 246 | — |
| 40 " " | 176 | 203 | 226 | 262 | 282 | 293 | 270 | 288 | 257 | 267 | 238 | 211 |
| 50 " " | — | — | 201 | 255 | 276 | 278 | — | — | 247 | 276 | — | — |
| 60 " " | 179 | 213 | — | — | — | — | — | — | — | — | — | — |
| 80 " " | 182 | 206 | — | — | — | — | — | — | — | — | — | — |
| *Elongation at break* (per cent.) | | | | | | | | | | | | |
| 5 min. at 142°C. | — | — | — | — | — | — | 860 | 812 | — | — | 625 | 650 |
| 10 " " | — | — | 887 | 792 | — | 882 | 823 | 777 | 765 | 750 | 625 | 648 |
| 20 " " | 853 | 773 | 855 | 782 | 810 | 792 | 705 | 690 | 682 | 722 | 568 | 650 |
| 30 " " | 858 | 800 | 840 | 753 | 765 | 760 | 663 | 677 | 695 | 727 | 650 | — |
| 40 " " | 855 | 790 | 787 | 742 | 747 | 742 | 657 | 670 | 707 | 735 | 655 | 643 |
| 50 " " | — | — | 792 | 703 | 748 | 732 | — | — | 713 | 745 | — | — |
| 60 " " | 845 | 792 | — | — | — | — | — | — | — | — | — | — |
| 80 " " | 858 | 798 | — | — | — | — | — | — | — | — | — | — |
| Mooney viscosity of compounded stock | 53 | 91 | 58 | 95 | 50 | 83 | 45 | 75 | 44 | 77 | 51 | Precured in Mooney |

## Discussion of Compounding Data

It is evident from the results that with some types of pure gum compounding, particularly those giving low or medium modulus vulcanisates, a considerable increase in modulus can be achieved by reducing the breakdown of the rubber to a minimum during compounding. However, as the acceleration is modified to give high modulus vulcanisates, a marked decrease in the sensitivity of the modulus to the viscosity of the uncompounded stock takes place; and with considerable boosting the modulus cannot be further increased by reducing breakdown of the rubber. It is proposed to apply the technique of nitrogen-compounding to carry out investigation over a wide range of stock plasticity, and it will be of interest to determine how far the above conclusions are borne out, both with pure gum types and with compounds containing fillers.

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