A. ACTION OF POTASSIUM CYANIDE
ON CERTAIN DISULPHIDES

B. BEHAVIOUR OF PURE CAOUTCHOUC

(A) The Action of Potassium Cyanide on Certain Disulphides.

(B) Some Aspects of the Behaviour of Pure Caoutchouc with Special Reference to the Influence of Proteins.

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A Thesis submitted in partial fulfilment
of the requirements for the degree,

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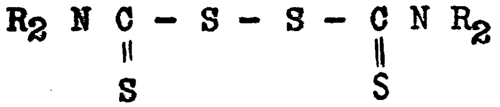
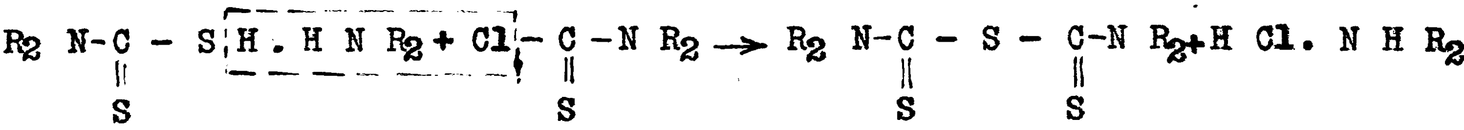
Historical

In 1903 Von Braun and Stechele[1] showed that thiuram disulphides on treatment with potassium cyanide were converted into the corresponding thiuram monosulphides. They found that on adding the cyanogen halides and also potassium cyanide to solutions of thiuram disulphides whose general formula may be written,



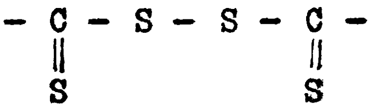
$$R_2N\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}NR_2$$

substances of the empirical formula $S_3C_2(NR_2)_2$ were obtained, generally with the production of intense yellow colour, and appearance in the solution of large quantities of thiocyanic acid. The supposition that the new products obtained were thiuram monosulphides was found to be correct when Von Braun successfully synthesized the compounds by making use of the reaction between dithiocarbamic acid salts and thiocarbamin chlorides thus



$$R_2N-\underset{\underset{S}{\|}}{C}-S\boxed{H\cdot HNR_2+Cl}-\underset{\underset{S}{\|}}{C}-NR_2\rightarrow R_2N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-NR_2+HCl\cdot NHR_2$$

Von Braun pointed out the need of an explanation for this reaction since it seems incomprehensible that a molecule of potassium cyanide should be capable of withdrawing one atom of sulphur from a structure as represented by the accepted formulation.



$$-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-$$

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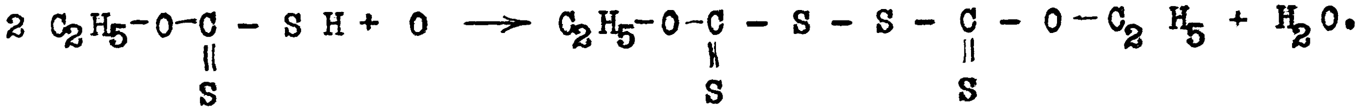
[1] Berichte, 36 2275.

He offered no explanation of the mechanism of this reaction and this question has not been solved since.

Theoretical

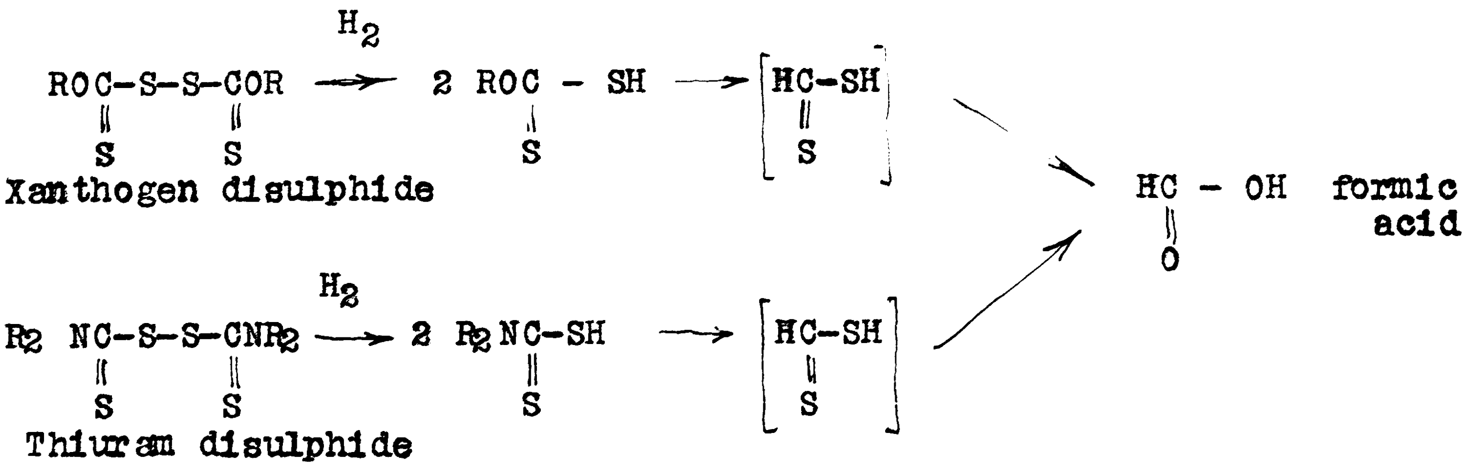
The above facts suggested a similar reaction with the disulphide derived from the oxidation of ethylxanthic acid



$$2\ C_2H_5-O-\underset{\underset{S}{\|}}{C}-SH + O \longrightarrow C_2H_5-O-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-O-C_2H_5 + H_2O.$$

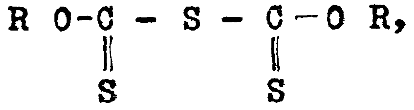
which, as may be seen, has the same disulphide structure as the thiuram disulphides (I). The belief that this reaction should proceed was further strengthened by the fact that ordinary disulphides R-S-S-R, such as diphenyl disulphide, benzyl disulphide, etc., were found to be unattacked by potassium cyanide even after prolonged heating. It appeared that the conversion of a di- to a monosulphide by treatment with potassium cyanide was made possible only through the particular configuration of these disulphides.

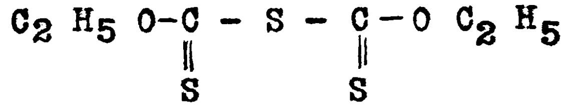
Another fact which indicated the probable production of monosulphides derived from ethylxanthic acid and possibly from its homologues was that the thiuram disulphides and "xanthogen" disulphides can both be regarded as derived from formic acid as may be seen from the following diagramatic scheme



From the above genealogical outline of the two types of compounds in question it becomes apparent that the xanthic acids are alkyl-oxy derivatives of the hypothetical dithioformic acid and the dithiocarbamates are the substituted amino derivatives of dithioformic acid.

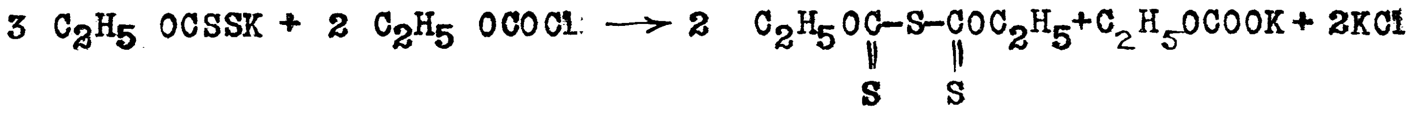
Since, as is shown above, these bodies are in reality very closely related, the reaction between the xanthogen disulphides and potassium cyanide was regarded as a very probable one and as will be shown later was actually carried out with a large number of the homologues of ethyl xanthogen disulphide.

This success led to the preparation of a number of the new alkyl-xanthogen monosulphides  $R\ O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O\ R$, a description of which this thesis contains.

Of the xanthogen monosulphides[1] obtained up to the time of this work, the ethyl compound  $C_2H_5\ O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O\ C_2H_5$

was the only member of this series known.

This was obtained by Welde[2] by treating potassium ethylxanthate and ethylchlorcarbonate (3 mol. to 2) whereby a very complicated reaction ensues according to the following equation:



$$3\ C_2H_5\ OCSSK + 2\ C_2H_5\ OCOCl \longrightarrow 2\ \ C_2H_5O\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}OC_2H_5 + C_2H_5OCOOK + 2KCl$$

After some preliminary work it was found that the product of the reaction of ethylxanthogen disulphide, and potassium cyanide gave an

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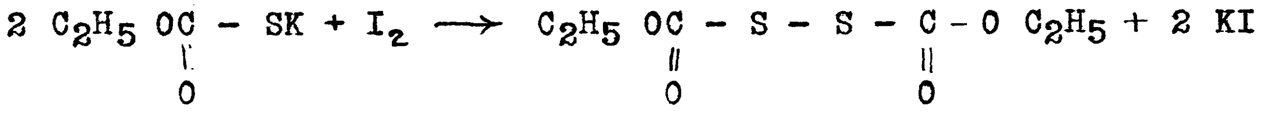
I. These are also called, Bis (thione carboxyl) sulphide alkyl esters.

2. Jour. für Pract. Chem. (2) 15 45.

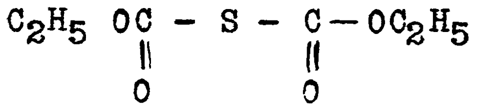
identical product melting at 52.5 - 53°C. (Welde 55°C).

The reaction in question was also found to go in the case of ethylcarbonsulphide[1], which is prepared by treating the potassium salt of ethylthiolcarbonic acid[2] - "Bender's Salt" - with iodine in the ordinary way.



$$2\ C_2H_5\ O\underset{\underset{O}{\|}}{C} - SK + I_2 \longrightarrow C_2H_5\ O\underset{\underset{O}{\|}}{C} - S - S - \underset{\underset{O}{\|}}{C} - O\ C_2H_5 + 2\ KI$$

on treating it with potassium cyanide this disulphide



$$C_2H_5\ O\underset{\underset{O}{\|}}{C} - S - \underset{\underset{O}{\|}}{C} - OC_2H_5$$

was converted smoothly to the corresponding monosulphide as described in the experimental part.

Of the aromatic or aryl-oxy derivates of dithioformic acid, the only alcohol which gave promising results was benzyl alcohol. These were only investigated in a qualitative way and no definite conclusions can be drawn. As far as can be judged from some preliminary tests the indications are that benzylxanthogen disulphide can be partially desulphurized by potassium cyanide to the corresponding monosulphide.

It seems of some importance in this work to arrive at some interpretation of the mechanism of this reaction since this does not seem to proceed in a straightforward manner and similar examples are not to be found.

The preparation by the action of oxidizing agents (e.g. iodine) in compounds containing the thiol group - SH clearly points to the structure X - S - S - X for disulphides, but it is proposed that

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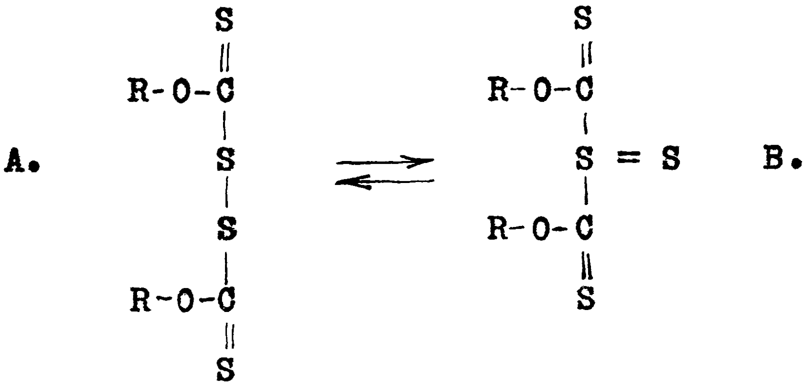
[1] Debus Annalen 75 142.

[2] Bender Annalen 148 137.

the molecule of these disulphides exist in two tautomeric forms which may be represented by



and that an equilibrium exists between the A and B forms. This explains the structure of the monosulphides and also the ease with which a sulphur atom, attached to sulphur entirely, may be withdrawn from the molecule. This view is supported by Kuster and Heberlein's[I] work on the constitution of the polysulphides of the alkali metals, wherein these workers came to the conclusion that these polysulphides have the general formula, $M_2 = S.S_x$ which Holmberg[2] maintains is also the general formulation of the alkyl polysulphides.

According to Holmberg then, ethyldisulphide should be written $C_2H_5 - \underset{\overset{\|}{S}}{S} - C_2H_5$ and not $C_2H_5 - S - S - C_2H_5$ although these disulphides are prepared by the oxidation of mercaptans.

The writer believes that the reason why such simple alkyl disulphides are not partially desulphurized by potassium cyanide to give thio-ethers is due to the influence of the alkyl groups (or aryl, in the case of aryl disulphides), and that if these substituents are replaced by a residue like $\left[R\ O\ \underset{\overset{\|}{S}}{C}\right]$ the strength of

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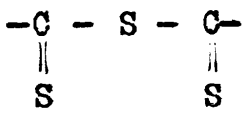
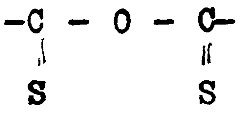
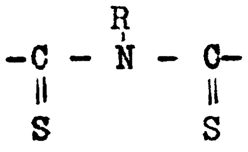
I. Zeitschr. f. anorg. Chem. 43 53.
2. Annalen 359. 81

the bond between the two sulphur atoms is weakened to such an extent that potassium cyanide under those conditions is capable of oxidizing itself to the thiocyanate.

As a proof of this it was found that although di-benzyl disulphide is not affected by this reducing agent the corresponding tetrasulphide is reduced completely to the disulphide, the presence of thiocyanate ions being easily demonstrable in the reaction mixture. The reaction in this case, however, differs from the reaction in question in that, in the former, di- and also poly-xanthogens are reduced to the monosulphides, while in the latter case reduction goes only as far as the disulphide stage.

It may be noted also that in the proposed equilibrium the B form must predominate to a large extent since the desulphurization takes place instanteously (with evolution of heat) whereas if the equilibrium was the other way about it would take an appreciable time for one form to change into the other during the reaction.

It is interesting to note that while thiuram disulphides and most bis (thione carboxyl) disulphide alkyl-esters are colorless, their corresponding mono-sulphides are all intensely golden yellow, indicating that possibly the grouping  $-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-$ is responsible for the colour.

Similar groupings such as  $-\underset{\underset{S}{\|}}{C}-O-\underset{\underset{S}{\|}}{C}-$ found in the thio carbamin-oxides[1] $O(CS.NR_2)_2$, and  $-\underset{\underset{S}{\|}}{C}-\overset{\overset{R}{|}}{N}-\underset{\underset{S}{\|}}{C}-$ found

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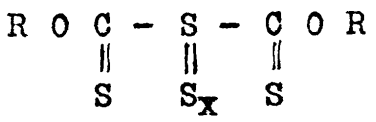
1. Billeter Berichte 20 1629.

in the substituted dithiobiurets[I] $RN(CSNR_2)_2$ invariably give yellow compounds.

Many side issues bearing on this problem have not been worked out owing to lack of time, for instance (a) the search of other types of molecules which lend themselves to the desulphurizing action of potassium cyanide; (b) the action of other reducing agents; (c)the effect of more than one molecule of potassium cyanide per molecule of dixanthogen. (From the writer's experience it seems that some complicated side reactions take place since in some cases where excess potassium cyanide was added, dark coloured solutions were obtained, especially after a lapse of a few hours); and (d) the action of one, two, three and more molecules of potassium cyanide on the xanthogen polysulphides whose general formula may be written



$$RO\underset{\underset{S}{\|}}{C} - \underset{\underset{S_X}{\|}}{S} - \underset{\underset{S}{\|}}{C}OR$$

where X may have a value up to four.

Of other possible molecules which would react with potassium cyanide, it seems that benzomercapto thiazol disulphide should undoubtedly react because it may readily be seen that the carbon atoms holding the sulphur are attached to nitrogen as in the thiuram disulphides and also to sulphur as in both the xanthogens and the thiuram disulphides. In other words, it is only a cyclic thiuram

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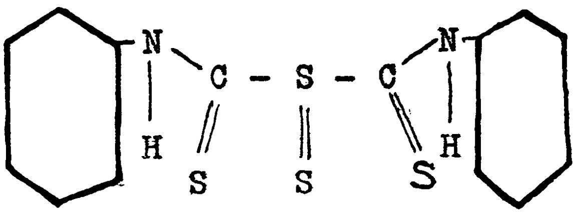
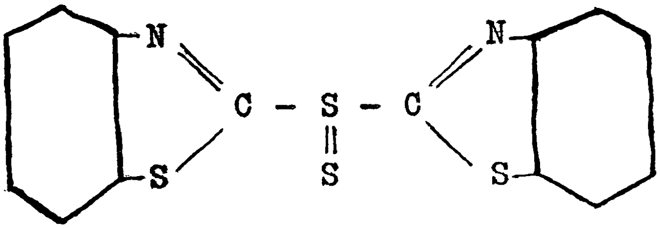
[I] Billeter Berichte 21 102. 26 1681

disulphide as may be seen from the two following formulations:-



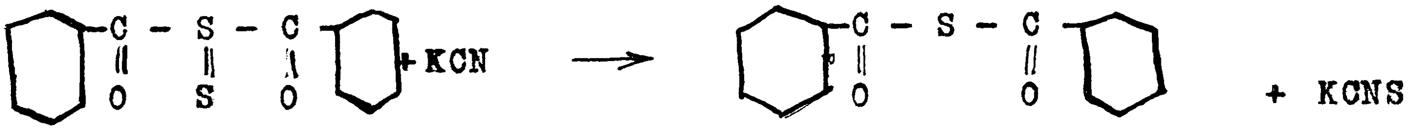
di-phenyl thiuram disulphide



benzo mercapto thiazol disulphide

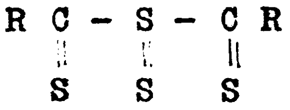
Although the nitrogen and sulphur atoms form part of a ring system still both these structural influences should lead to a positive result.

Benzoyl disulphide[I] seems to be another compound which should react with potassium cyanide to give benzoyl monosulphide.



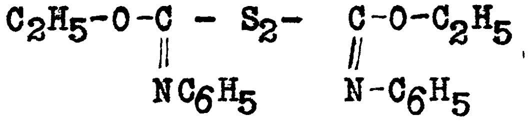
Other compounds which it is proposed to subject to the action of potassium cyanide later are:-

(a) Di-thio acyl disulphides



$R\underset{\overset{\|}{S}}{C} - \underset{\overset{\|}{S}}{S} - \underset{\overset{\|}{S}}{C}R$ and

(b) the disulphides from thiourethanes, e.g.



$C_2H_5-O-\underset{\overset{\|}{NC_6H_5}}{C} - S_2 - \underset{\overset{/\!/}{N-C_6H_5}}{C}-O-C_2H_5$

It is not difficult to confirm by synthesis the structure of the monosulphides which have been obtained by the action of potassium cyanide on disulphides. The synthesis of the bis (thione carboxyl) sulphide ethyl ester might for example be worked out in an

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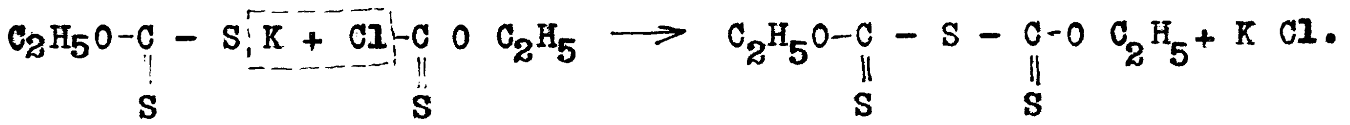
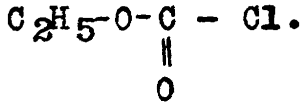
[I] Engelhardt, Malyschew and Latschinow. Zeitschrift für Chemie 1868 357.

analogous way to Von Braun's method of arriving at the constitution of the thiuram monosulphides,[1] namely by treating potassium ethyl xanthate with the acid chloride of ethyl xanthic acid in the following way:-



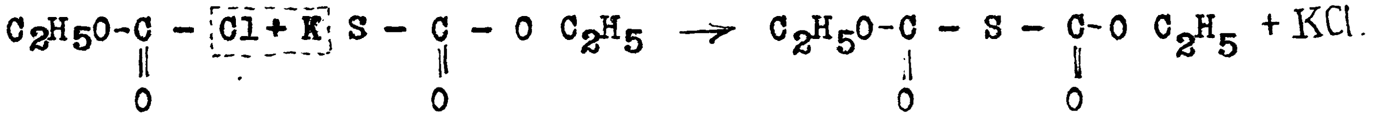
$$C_2H_5O-\underset{\underset{S}{|}}{C}-S\boxed{K+Cl}-\underset{\underset{S}{\|}}{C}\;O\;C_2H_5 \longrightarrow C_2H_5O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O\;C_2H_5+K\,Cl.$$

This acid chloride, however, is very difficult to obtain, and involves the use of thio-phosgene for its preparation which at present is procurable only in Germany. It was found however that the synthesis of the analogous bis (thiol carboxyl) sulphide ethyl ester may be very simply carried out using the oxygen analogue of the acid chloride of ethyl xanthic acid namely ethyl chlorcarbonate



$$C_2H_5-O-\underset{\underset{O}{\|}}{C}-Cl.$$

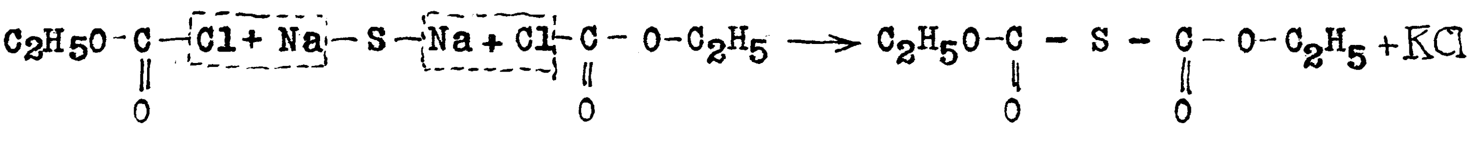
The reaction is represented thus -



$$C_2H_5O-\underset{\underset{O}{\|}}{C}-\boxed{Cl+K}\;S-\underset{\underset{O}{\|}}{C}-O\;C_2H_5 \longrightarrow C_2H_5O-\underset{\underset{O}{\|}}{C}-S-\underset{\underset{O}{\|}}{C}-O\;C_2H_5+KCl.$$

I II III

This compound (III) was prepared many years ago by V.Meyer[2] by acting on ethyl chlor carbonate with sodium disulphide.



$$C_2H_5O-\underset{\underset{O}{\|}}{C}-\boxed{Cl+Na}-S-\boxed{Na+Cl}-\underset{\underset{O}{\|}}{C}-O-C_2H_5 \longrightarrow C_2H_5O-\underset{\underset{O}{\|}}{C}-S-\underset{\underset{O}{\|}}{C}-O-C_2H_5+KCl$$

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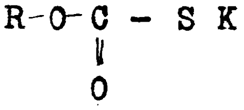
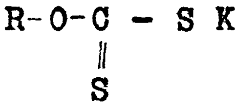
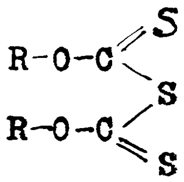
[1] See page 1.

[2] Berichte 2 298.

The compound obtained by either method corresponded entirely with the compound obtained by the reduction with potassium cyanide and from the similarity in structure between the thiol carbonates  $R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{ - }S\ K$ and the xanthates  $R\text{-}O\text{-}\underset{\underset{S}{\|}}{C}\text{ - }S\ K$ it is permissable to accept the structure of the bis (thione carboxyl) sulphide esters as



Experimental

To test the action of potassium cyanide on aryl disulphides, phenyl disulphide was made as indicated by Hubner and Alsberg.[1] The melting point of this compound was 61.5°C.

One molecule (5 grams) of phenyl disulphide and one nolecule (1.48 g) of potassium cyanide were refluxed with 50 c.c. of alcohol for one hour. That some reaction took place was apparent from the odour and colour of the reaction product. The colour turned to dark reddish brown and the liquid smelt of thiophenol. On diluting with water almost all the original disulphide was precipitated. After purification it melted at 62°C.

On repeating the above experiment using two equivalents of potassium cyanide, a reaction seemed to take place since small amounts of an ammonium compound separated in the condenser and

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1. Annalen 156 330.

thiophenol was present in the solution after acidification.

From the above experiments it is concluded that under these conditions phenyl disulphide is not converted to the monosulphide by the action of potassium cyanide.

The action of potassium cyanide was also investigated in the case of benzyl disulphide, the results being negative. Von Braun[1] also reports that benzyl disulphide remains unaltered by boiling with the cyanides of sodium or potassium.

After this preliminary work on the ordinary type of disulphides it was decided to investigate the action of potassium cyanide on the bis (thione carboxyl) disulphide alkyl esters or "Dixanthogens" as we have chosen to call these bodies.

Action of Potassium Cyanide on Ethyl Dixanthogen.

Ten grams of ethyl dixanthogen[2] were dissolved in about 100 c.c. of alcohol (95%) and 2.69 grams (1 mol.) of potassium cyanide dissolved in the least amount of water and diluted with alcohol, were added at once. A deep yellow colour was developed immediately and some dixanthogen which remained undissolved in the alcohol soon went into solution. This was refluxed for one hour. At the end of this period a dark reddish coloured solution was obtained which on diluting with water yielded an oil which could not be solidified. A solid product was sought since it was expected that the monosulphide obtained should have a higher melting point than the disulphide because

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1. Berichte 36 2275
2. Desains Jahrsbericht uber die Forschriftte der Chemie 1847/48, 690.

the bis (thione carboxyl) sulphide ethyl ester prepared by Welde had a melting point of 54°C.

The same experiment was repeated, only the reaction was carried out at 50° C for one hour. On adding water to this, a yellow oil was obtained which on keeping solidified, but not completely, thus indicating that a still lower temperature should be utilized for the reaction.

Accordingly 5 grams ethyl dixanthogen were treated in the usual way with 1.34 grams of alcoholic potassium cyanide. The reaction was allowed to proceed at room temperature for fifteen minutes. On isolating the yellow product it was found to be a very low melting substance from which after several recrystallizations from alcohol a small quantity of a bright yellow solid was obtained having a melting point of 52° C. This must therefore be the bis (thione carboxyl) sulphide ethyl ester. A mixed melting point with Welde's substance showed no depression.

It was finally decided to try this reaction in the cold. By keeping the temperature between 0° and 5° C, an 89% yield of crude monosulphide was obtained, this having a melting point of about 45° C. (5 g $(C_2H_5O\ C\ S)_2S_2$ gave 3.59 g $(C_2H_5O\ C\ S)_2S$.). On recrystallization from aqueous alcohol a pure sample of bis (thione carboxyl) sulphide ethyl ester can be obtained.

Sulphur determination

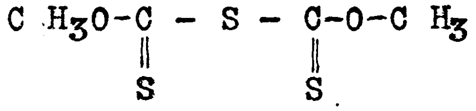
.1754 g. subst. gave .5835 g. $Ba\ S\ O_4$

Percent sulphur. Found 45.75. Calculated for $(C_2H_5O\ C\ S)_2S$ 45.72

Methyl Dixanthogen[1]

Desains obtained this compound as a yellow oil. However by freezing a small sample of this in a carbon dioxide-ether freezing mixture, it began to crystallize and on "seeding" a carefully purified sample of methyl dixanthogen it solidified rapidly to an almost colourless solid, melting at 20.7C. On recrystallization from alcohol the compound was obtained as a colourless mass of crystals melting at 22°- 22.3°C.

Bis (thione carboxyl) sulphide methyl ester.



$$CH_3O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O-CH_3$$

This was obtained by treating 15 grams of methyl dixanthogen in about 75 c.c. of alcohol with 4.56 grams of potassium cyanide in 10 c.c. of water and 10 c.c. of alcohol. The reaction was carried out at 10° C for about one hour and on throwing the product out of solution with water an oil was obtained. This oil after careful washing was separated as much as possible from water and dried in a vacuum desiccator over sulphuric acid. The dried product did not solidify but on "seeding" a little with a crystal of ethyl xanthogen monosulphide, crystallization set in but the whole mass did not solidify. From the whole reaction product 2.2 grams of fine yellow needles were obtained having a melting point of 55° C.

Analysis - .1650 g. subst. gave .5990 g. Ba SO_4
Per cent Sulphur Found 49.5. Calculated for $(CH_3OCS)_2S$ 50.5

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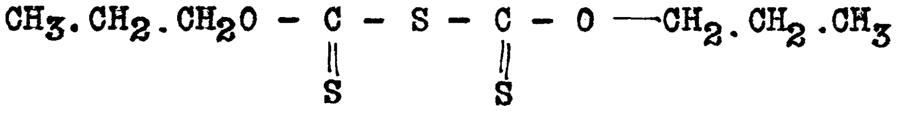
[1] Jahrsbericht fur die forschritte der Chemie 1847/48. 674.

N-Propyl Dixanthogen[I]

Normal propyl potassium xanthate (150 grams) were treated with aqueous iodine as long as the iodine was absorbed. During the reaction, which was carried out with mechanical stirring, a reddish brown oil separated out. Slight traces of iodine were removed with sodium thiosulphate solution. This oil was well washed with water to remove potassium iodide and the wet oil finally dried in vacuo over sulphuric acid. By this method (which is used for the preparation of all dixanthogens) 100 grams of crude n-propyl dixanthogen was obtained. An attempt to obtain a crystalline product by freezing in carbon dioxide-ether freezing mixtures failed. It seems that the melting point of this compound must lie below 5°C.

Bis (thione carboxyl) sulphide n-propyl ester



$$CH_3.CH_2.CH_2O - \underset{\underset{S}{\|}}{C} - S - \underset{\underset{S}{\|}}{C} - O — CH_2.CH_2.CH_3$$

To prepare this substance, 30 grams of n-propyl dixanthogen were dissolved in about 150 c.c. of 95% alcohol and 7.26 grams potassium cyanide (1 mol) in water and alcohol, were added with cooling and mechanical stirring. The dixanthogen immediately lost its dark colour and gave a light yellow solution. After reacting for about one hour it was diluted with water and isolated in the ordinary way. This is a dark yellow oil, and as the corresponding disulphide could not be made to crystallize and a distillation under vacuo was unsuccessful, due to the decomposition at about 20 mm. of

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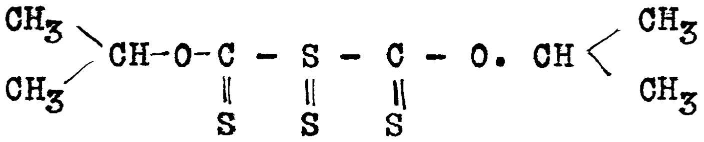
[I] Scala. Gazetta Chimica It. <u>17</u> 80.

mercury, it being impossible to maintain a lower vacuum.

Analysis - .1757 grams subst. gave .5270 Ba SO_4

Percent Sulphur. Found 40.05. Calculated for $(C_3H_7O\ C\ S)_2S$ 40.33

Iso-Propyl Dixanthogen[I]

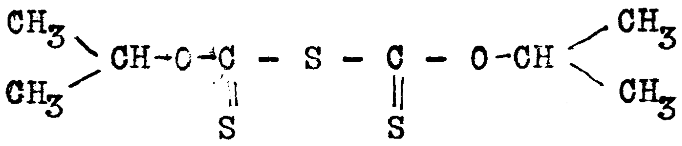


This substance is not described in the literature and its preparation may be carried out in exactly the same way as the other dixanthogens. About 100 grams of potassium isopropyl xanthate are dissolved in water. A considerable temperature drop occurs as is usual with very soluble substances. A strong solution of iodine in aqueous potassium iodide is now gradually added with vigorous stirring (mechanical) until a slight excess of iodine is present. This excess may be removed by small amounts of the potassium xanthate or with dilute sodium thiosulphate solution. In this way an almost theoretical yield of the dixanthogen is obtained as a colourless crystalline substance. Two recrystallizations from alcohol are sufficient to give a very pure product melting at 58 - 58.5°C.

Analysis - .0894 g. substance gave .3072 g. Ba S O_4
Percent Sulphur found 47.23 Calculated for $(C_3H_7O\ C\ S)_2S_2$ 47.45.

I. This substance may also be called
Bis [(iso-propyl oxy)-(thio formyl)] disulphide.

Bis (thione carboxyl) sulphide iso propyl ester



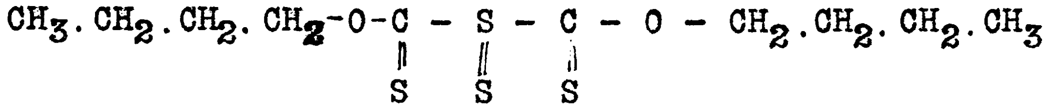
This substance was prepared by reacting with 3.63 grams potassium cyanide in water and alcohol on 15 grams of the iso propyl dixanthogen described above. The reaction is complete in a few minutes, a golden yellow mass of crystals separates out which after recrystallization from alcohol melts at 52 - 54°C.

Analysis:
.2001 g. subst. gave .1220 g. H_2O and .2932 g. CO_2

Calculated for $C_8H_{14}O_2S_4$	Found
H = 5.88%	6.77%
C = 40.20%	40.10%

It should be pointed out that great difficulties are encountered in attempting to analyse for carbon and hydrogen by the ordinary combustion method. This is due to the large percentage of sulphur in these compounds. It was found necessary to use alternate sections of copper oxide and lead chromate, and to heat very strongly (except the front of the tube) before concordant results were obtained. The somewhat high value for hydrogen may be attributed to the high heat used rendering the lead sulphate formed unstable and decomposing into the sulphur oxides which might have been absorbed in the sulphuric acid absorption tube.

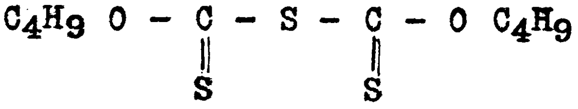
N-Butyl Dixanthogen



$$CH_3.CH_2.CH_2.CH_2-O-\underset{\underset{S}{\|}}{C}-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{C}-O-CH_2.CH_2.CH_2.CH_3$$

This was obtained in exactly the same way as the other dixanthogens. It is a reddish brown oil which it was not possible to crystallize even after intense cooling. This compound is also not described in the literature. It was found impossible to distil these compounds except at exceedingly low pressures otherwise decomposition takes place, giving amongst other things the corresponding esters of the xanthic acid used, that is, in this case, n-butyl ester of butyl xanthic acid $C_4H_9O\ C\ S\ S\ C_4H_9$ would be obtained. The density was determined at 22°C and was found to be 1.158.

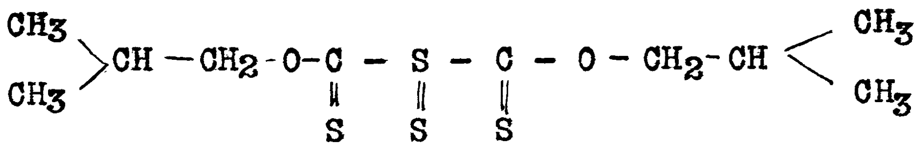
Bis (thione carboxyl) sulphide n-butyl ester



$$C_4H_9\ O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-O\ C_4H_9$$

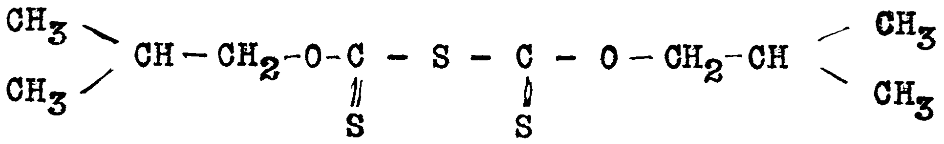
On treating one molecule of the dixanthogen with one molecule of potassium cyanide in the ordinary way, the dark colour of the n-butyl dixanthogen disappears and a monoxanthogen is obtained in good yield having a dark yellow colour. As in the previous cases this oil did not solidify even after keeping for some months and decomposition occurs on attempting to redistil it. The density at 22°C is 1.121.

Iso Butyl Dixanthogen[1]



Mylius[1] obtained this compound by the action of chlorine gas on the corresponding potassium iso-butyl xanthate. It was found that oxidizing with iodine gives much more uniform products and lessens, to a minimum, the chance of side reactions occurring. Using the iodine method a light yellow oil was obtained which could not be crystallized below -10° C. This is in accordance with Mylius' observation on this body. The density at 22°C is 1.173.

Bis (thione carboxyl) sulphide iso-butyl ester.



This was obtained from the corresponding dixanthogen in the ordinary way. This is also a golden yellow oil unstable to heat even at very low pressures. Density at 22°C is 1.126.

In the same manner as described in the foregoing pages the iso-amyl dixanthogen and the corresponding bis (thione carboxyl) sulphide iso-amyl ester were prepared. These did not present any marked differences in behaviour and general properties from the other hemologes.

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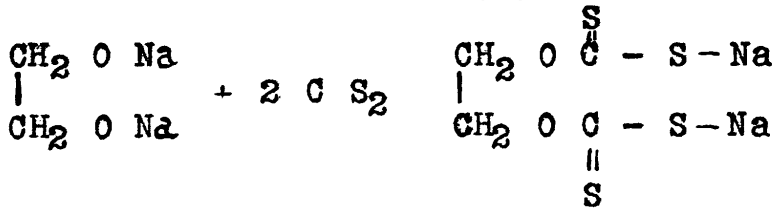
[1] Mylius Berichte 5 976.

The following experimental details cover many of the unsuccessful attempts to prepare dixanthogens and the corresponding monosulphides from them. These include some of the products derived from cyclic alcohols such as furfuryl, cinnamic and benzyl alcohols and also one dihydric alcohol namely ethylene glycol.

In most cases xanthates are obtainable and sometimes even dixanthogens which are very unstable rendering the work very difficult. This however does not mean that monoxanthogens are not possible, it only being a case of proper control of the physical conditions of the experiments.

Ethylene glycol was the only polyhydric alcohol chosen for the extension of this work. Since no mono- or di-xanthate had previously been prepared it was necessary to investigate the possibility of preparing these compounds. To do this, the first reaction which occurred to us was the preparation of the di-xanthate through the disodium derivative of the glycol thus



$$\begin{array}{l} CH_2\ O\ Na \\ | \\ CH_2\ O\ Na \end{array} + 2\ C\ S_2 \qquad \begin{array}{l} CH_2\ O\ \overset{S}{\overset{\|}{C}} - S - Na \\ | \\ CH_2\ O\ \underset{S}{\underset{\|}{C}} - S - Na \end{array}$$

Accordingly the di-sodium alcoholate was made according to the method of Forcand[1]. This was suspended in excess ethylene alcohol and carbon disulphide added. This method after some experimentation gave no results.

However, on dissolving potassium hydroxide in excess boiling ethylene glycol and then adding carbon disulphide evidence of a reaction was shown for heat was soon developed and a light yellow

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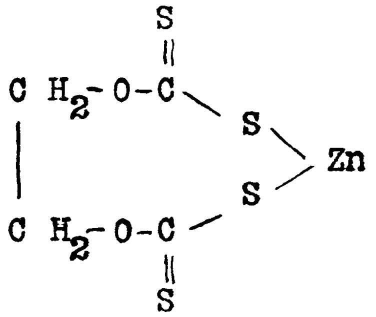
[1] Comptes Rendus t 113 1048.

solid separated in a reddish solution. This solid which was presumably the mono or di-potassium xanthate reacted with iodine and gave an oil which after standing for some days, solidified. This product however seems to be a mixture of various products which render it very difficult to investigate.

The nearest approach to a definite compound was made by dissolving the di-sodium glycollate in alcohol (ethyl) and adding two equivalents of carbon disulphide. After some time ether was added and the yellow oil obtained allowed to stand for two days when it solidified completely. This solid appeared to be heterogeneous under the microscope and it was found that a fraction could be extracted with acetone. The fraction obtained is an oil which also solidified on standing. It was found that aqueous solutions of this gave a white amorphous precipitate with zinc chloride solution. Analysis for zinc in this compound gave a value which agreed fairly well with the value calculated for



Analysis - .1859 grams subst. gave .0569 g. ZnO.

Percent zinc Found 24.6 Calculated for $C_4H_4O_2S_4$ Zn 23.6%.

This work was not pursued any further owing to lack of time.

Cinnamic alcohol was the next substance to offer difficulties which could not be overcome for the time being. The first, and as a matter of fact, the only difficulty was in the preparation of the potassium salt of cinnamyl xanthic acid.

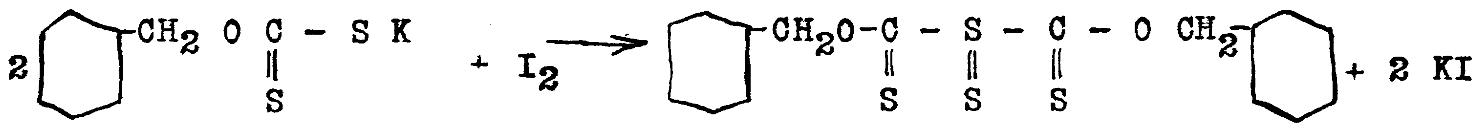
$C_6H_5-CH = CH - CH_2\ O\ C\ S\ S\ K.$

An attempt to prepare the cinnamyl, alcoholate by dissolving metallic potassium in the alcohol gave no results. Using Forcand's[1] method of preparing sodium salts of high boiling alcohols,

$$R\ O\ H + C_2H_5\ O\ Na \longrightarrow R\ O\ Na + C_2H_5\ O\ H.$$

gave no definite products and the work was discontinued.

Nametkin and Kursanoff[2] found that benzyl alcohol gives rise to a xanthogenic acid, the potassium salt of which is quite stable. Accordingly, a dixanthogen was attempted by adding an aqueous solution of iodine (in potassium iodide) to a water solution of the potassium benzyl xanthate.



By this proce~~e~~dure a yellow oil was obtained which after strong cooling in a carbon-dioxide-ether mixture began to crystallize. It was found, however, that this dixanthogen is not stable at the temperature of boiling alcohol from which it was attempted to crystallize it. By dissolving it in hot alcohol sulphur is found to separate leaving behind a red heavy oil of uncertain composition. The work on this compound was suspended due to lack of materials. Nevertheless since the dixanthogen is capable of existance (at room temperature) it seems very likely that this compound should be capable of partial desulphuration yielding the bis (thione carboxyl) sulphide benzyl ester.

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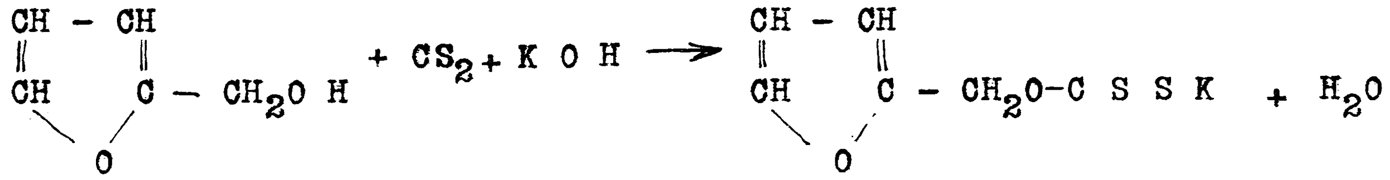
[1] loc. cit.

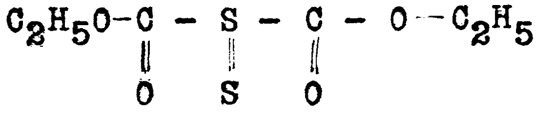
[2] Jour. fur. pract. Chemie 112 164.

It was found that furfuryl alcohol yielded a hitherto unknown xanthogenic acid. This is very easily obtained by adding one molecule of aqueous potassium hydrate to a solution of one molecule of carbon disulphide in one equivalent of furfuryl alcohol.



On treating this potassium salt with iodine decomposition occurs immediately giving a dark amorphous powder, a very dark red oil and an evolution of gas, probably carbon-oxy-sulphide.

Dixanthogen from ethyl thiol carbonic acid.



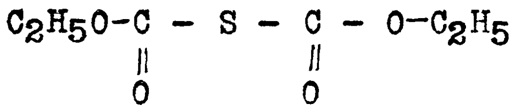
$$C_2H_5O-\underset{\underset{O}{\|}}{C}-\underset{\underset{S}{\|}}{S}-\underset{\underset{O}{\|}}{C}-O-C_2H_5$$

This body was prepared by oxidizing potassium ethyl thiol carbonate with aqueous iodine according to the method described by Debus.[1] This is an almost colourless oil with a very pleasant ethereal odor.

Analysis
.1904 g. subst. gave .4170 $Ba\ S\ O_4$

Percent sulphur Found 31.0 Calculated for $(C_2H_5O\ C\ O)_2S$ 30.5.

Monoxanthogen from -ethyl carbon sulphide[2]



$$C_2H_5O-\underset{\underset{O}{\|}}{C}-S-\underset{\underset{O}{\|}}{C}-O-C_2H_5$$

When one molecule of the dixanthogen - ethyl carbon sulphide - is dissolved in alcohol and treated with potassium cyanide (1 mol.), appreciable heat is developed unless precaution is taken to cool the reaction flask. After about 15 minutes the oil was thrown out with water, washed well and dried in a desiccator. The oil obtained has a slight yellow tinge and smells not at all unpleasant.

A sulphur determination gave 17.95 per cent sulphur whereas that calculated for $(C_2H_5O\ C\ O)_2S$ is 17.98%. The density of this compound was found to be 1.158 at 23°C.

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[1] Annalen 75 142.

[2] Also called ethyl ester of thio dicarbonic acid.

Synthesis of ethyl ester of thio dicarbonic acid.

About 60 grams of potassium ethyl thiol carbonate are suspended in 350 c.c. of ether and 50.5 grams of ethyl chlor carbonate added. On standing for about half an hour sufficient heat is developed to cause the ether to boil quietly. It is therefore placed under a well cooled reflux condenser. This boiling stopped in about an hour. The reaction mixture was then gently heated (under reflux) for two more hours after which time all traces of ethyl chlor carbonate disappeared. The separated potassium chloride is then filtered off and the ether distilled. This procedure gave 57 g. of a light yellow oil having all the properties of the ethyl thio dicarbonate prepared by the desulphurization of ethyl carbon sulphide.

Analysis
.2535 g. subst. gave .3320 g. $BaSO_4$

Percent sulphur Found 17.93 Calculated for $(C_2H_5OCO)_2S$ 17.98

In connection with this synthesis it is interesting to note that Wheeler & Dustin[1] make the statement that they found it impossible to obtain any straightforward reaction between ethyl chlor carbonate and potassium xanthate or potassium ethyl thiol carbonate, but always obtained decomposition products. These experimenters describe their experimental work very inadequately e.g. "When 55 grams of potassium xanthate and 37 g ethyl chlor carbonate were allowed to react"..... Evidently these workers used no diluent and hence the various decomposition products due to the heat developed. In our work the temperature never rose above the boiling point of ether

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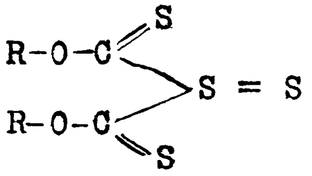
[1] Am. Chem. Jour. 24 443.

and as recorded above the synthesis was successfully accomplished.

Action of Potassium Cyanide on Benzyl Tetrasulphide.

This work was carried out to link up and also to confirm our theory of the structure of the dixanthogens. As may be remembered we postulated the following configuration for these compounds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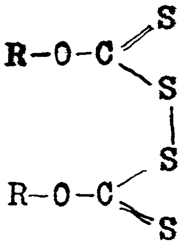
where the sulphur does not exist in a chain so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Also, it was our contention that the reason why aryl or alkyl disulphides do not lend themselves to partial desulphurization by potassium cyanide is due to the influence of these groups. If however polysulphides are treated it is found that these are desulphurized to the disulphide stage.

Benzyl tetrasulphide, was prepared by treating sulphur chloride with benzyl mercaptan in carbon tetrachloride[1]. This compound is a colourless substance very difficult to crystallize and melting at 49°C.

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[1] Smythe & Foster J. Chem. Soc. 97 1195.

Thomas and Jones[1], from their work on the action of the alkali polysulphides on organic halides came to the conclusion that tetrasulphides such as benzyl tetrasulphide are incapable of existence but immediately break down into benzyl disulphide and benzyl pentasulphide, according to the equation

$$3\ R_2S_4 \longrightarrow 2\ R_2S_5 + R_2S_2$$

This view that organic tetrasulphides are incapable of existence does not seem to be well founded since the arrangement of the sulphur atoms in sulphur chloride S_2Cl_2 may not be the same as in sodium tetrasulphide Na_2S_4. However the case may be it is certain that at least some, if not most of the product, consisted of polysulphides.

When 5 grams of the benzyl tetrasulphide was treated with alcoholic potassium cyanide (2 mols.), an immediate reaction took place whereby an intense yellow colour is developed which gradually faded, completely. On cooling and diluting the alcohol somewhat, with water, beautiful colourless crystals of benzyl disulphide melting at 70.5 to 71°C were obtained in an almost theoretical yield. The wash waters on addition of ferric ions turn an intense blood red colour thus indicating the oxidation of potassium cyanide to potassium thiocyanate.

Summary.

1. Potassium cyanide does not remove sulphur from phenyl disulphide or benzyl disulphide. It does, however, remove sulphur from benzyl tetrasulphide, converting the latter into benzyl disulphide.

$$C_6H_5CH_2\ S_4\ CH_2C_6H_5 + 2KCN \longrightarrow C_6H_5CH_2\ S_2\ CH_2C_6H_5 + 2KCNS$$

2. Potassium cyanide removes an atom of sulphur from the alkyl esters of thione-carboxyl disulphides, $RO-CS-S_2-CS-OR$, converting them into monosulphides, $RO-CS-S-CS-OR$. In this way the following new monosulphides have been prepared:-

$CH_3O\ CS\ S\ CS\ OCH_3$	m.p. 55°C
$C_3H_7O\ CS\ S\ CS\ OC_3H_7$ (normal)	liquid
$C_3H_7O\ CS\ S\ CS\ C_3H_7$ (iso)	m.p. 58°- 58.5°C
$C_4H_9O\ CS\ S\ CS\ C_4H_9$ (normal)	m.p. 52°- 54°C
$C_4H_9O\ CS\ S\ CS\ OC_4H_9$ (iso)	liquid
$C_5H_{11}\ O\ CS\ S\ CS\ OC_5H_{11}$ (iso)	liquid

Incident to this work, several new disulphides of the type $RO\ CS\ S_2\ CS\ OR$, and several new salts (potassium) of xanthic acids were prepared. Several disulphides were obtained as crystalline solids which were previously known only as liquids.

3. Potassium cyanide removes an atom of sulphur from the ethyl ester of carboxyl disulphide, $C_2H_5O\ CO\ S_2\ CO\ C_2H_5$, giving the corresponding monosulphide, $C_2H_5O\ CS\ S\ CO\ OC_2H_5$. The latter compound has also been synthesized by the following reaction:-

$$C_2H_5O-CO\ SK + Cl\ CO\ OC_2H_5 \longrightarrow C_2H_5O\ CO\ S\ CO\ OC_2H_5 + KCl$$

4. Inconclusive experiments were carried out on the xanthates and thione-carboxyl disulphides from benzyl alcohol, cinnamic alcohol, furfuryl alcohol, ethylene gylcol.
5. The bearing of the results on the matter of the constitution of the types of organic di- and poly- sulphides in question is discussed.

Some Aspects of the Behaviour of Pure Caoutchouc With Special Reference to the Influence of Protein.

(A Preliminary)

Introduction

Numerous investigators have worked on the effect of added substances, or even the influence of the naturally occurring impurities in rubber, on the properties both chemical and physical of vulcanized caoutchouc. Since many theories of the action of vulcanization accelerators[1] are based upon their interaction with the "resins" or "proteins" occuring in the rubber, while other theories concerning the physical structure of this material postulate a colloidal system in which the rubber is the disperse phase and the proteins and resins form the dispersion medium,[2] it seems of some importance to investigate the influence of various compounding ingredients, especially of various accelerators on protein- and resin- free caoutchouc to ascertain if the results obtained will bear out or disagree with the various theories proposed for rubber structure and accelerator action.

This brief report contains the preliminary work done on this problem.

I. C.W.Bedford & L.B.Sebrell Jour. Indust & Eng. Chem. 13 1034 & 14,25
Bedford & H.Gray Jour. Indust. & Eng. Chem. 15 720
H. Feucheter Kolloidchem. Beihefte 20 78 & 21 171.
Martin & Davey Jour. Soc. Chem. Ind. 44 317 - 320 T.

2. Hauser India Rubber Journal 68 19. 68 725
Review gen. colloids 3 289.
H.P.Stevens India Rubber Journal 70 1059.

Experimental

The naturally occurring impurities found in coagulated rubber are (a) oxygen containing compounds commonly known as "resins" and (b) nitrogen containing bodies referred to as "proteins." Before entering into an extensive survey of the influence on vulcanization of pure caoutchouc of other materials, it was decided to investigate the part played by these naturally occurring bodies, namely resins and proteins.

The method adopted for this was to extract ordinary commercial rubber with a solution of 70 parts acetone and 30 parts petrolic ether (by weight) for several days, the solution being renewed every twenty-four hours. This extraction is continued until no residue can be detected in an aliquot portion of the acetone extract. In this way all resinous materials are extracted leaving behind the proteins enmeshed in the rubber. It was found necessary to extract about five or six times before resin-free rubber could be obtained.

No direct method for dissolving out the proteins has so far been developed, so that it is found necessary to diffuse the caoutchouc out and leave the protein enmeshed in some of the swollen rubber which is not in solution. For this purpose light pretroleum ether was used. This was allowed to remain in contact with the rubber for about one month whereby a two per cent solution of rubber was obtained. This was carefully filtered from bits of undissolved rubber, and then precipitated with acetone, well squeezed and dried in vacuum desiccator until all entrapped solvent had escaped. By this procedure only 200 grams of protein-free material was obtained from about 4 pounds of commercial pale crepe. This small yield, however, was sufficient for a preliminary experiment.

This rubber is then put through the regular process for converting it into a vulcanized product, namely:

(a) Mixing
(b) Vulcanizing
(c) Testing.

As the machines required for these operations had only newly been secured, it was necessary to devote a good deal of time in installing them and developing a satisfactory technique.

The mixing operation is carried out on hot rolls to render the rubber sufficiently plastic to take up the sulphur and any other powders added. The rubber is always allowed to run around the front roll, continuously, being cut on the roll by means of a knife and folded over from time to time, while the compounding ingredients are being added.

All test pieces are vulcanized in moulds. For this purpose rectangular moulds were designed each to give two slabs of rubber 6" x 2.5" x 0.1". The moulds consist of two solid steel plates, one being hollowed out to the required depth. These plates are supplied with bolts and a hook. In all the experiments to be described, vulcanization was carried out at 115°C using a specially constructed paraffin oil bath. The moulds are suspended from the hooks supplied and subjected to the heat treatment for definite time intervals, after which they are rapidly withdrawn and immersed in cold water.

The rubber slabs obtained from the moulds after vulcanization are then cut into rings or straight test pieces, depending on the object of the experiment. These rings are cut by the Schopper Cutting Press constructed specially for this purpose. Three circular knives are provided. A disc is first cut from the rubber slab by means of the largest knife which is 56.9 mms. in diameter. The second largest knife is now substituted and the rubber disc cut by means of the largest knife is placed in a die into which it fits exactly, this die being fixed by means of screws into holes on the metal table beneath, so that it is concentric with respect to the cutting knives. This knife cuts a smaller disc and a ring from the large disc; this ring being irregular on its outer edge is discarded. The smaller disc, cut by the second knife, is then placed in a still smaller die into which it fits exactly and the smallest knife is substituted and another ring cut as before. This is the ring used for all tests. The difference in diameter between the two smallest knives is 8 mms., so that the cross sectional area of our test piece is $4 \times 2.54 = 10.16$ sq. mms. (approx.).

These rings are then stretched until they break on the Schopper Rubber Testing Machine. The stretching of the rubber is done by means of a piston driven by hydraulic pressure. The load is applied by means of a weighted lever moving against an arc graduated in kilograms. The load lever which moves against the graduated arc is arrested automatically when the test piece breaks.

The elongation is measured by determining the distance between the two rollers over which the rubber ring to be tested fits. The lower roller is attached to the piston and by means of a catch which is released automatically when the sample breaks it carries the extension scale with it. The upper roller is fixed to the load lever and carries a vernier. By means of an autographic arrangement consisting of a drum attached to the machine and connected by means of various pulleys and strings to the load lever and a pen connected to the extension piston, the stress and strain throughout a test is recorded as a continuous curve.

In this preliminary work it was proposed to make comparative tests on

(a) ordinary rubber (as a control)
(b) resin-free rubber
(c) resin-free rubber plus oleic acid.
(d) protein-free rubber plus oleic acid.

The object of adding oleic acid is that it takes the place of the extracted resins since it was found that the resins consist largely of fatty acids.[1]

A. <u>Commercial Pale Crepe</u>.

The mix consisted of 100 g. rubber
5 g. sulphur
5 g. zinc oxide ("kadox")
.5 g. zinc pentamethylenedithiocarbamate.

This was vulcanized at 115°C for 20, 30 and 40 minutes. Curves # 1 show very plainly the curves obtained with a progressive cure. It is apparent that although the strength of the vulcanizate does not increase with the duration of heating it nevertheless becomes much tougher.

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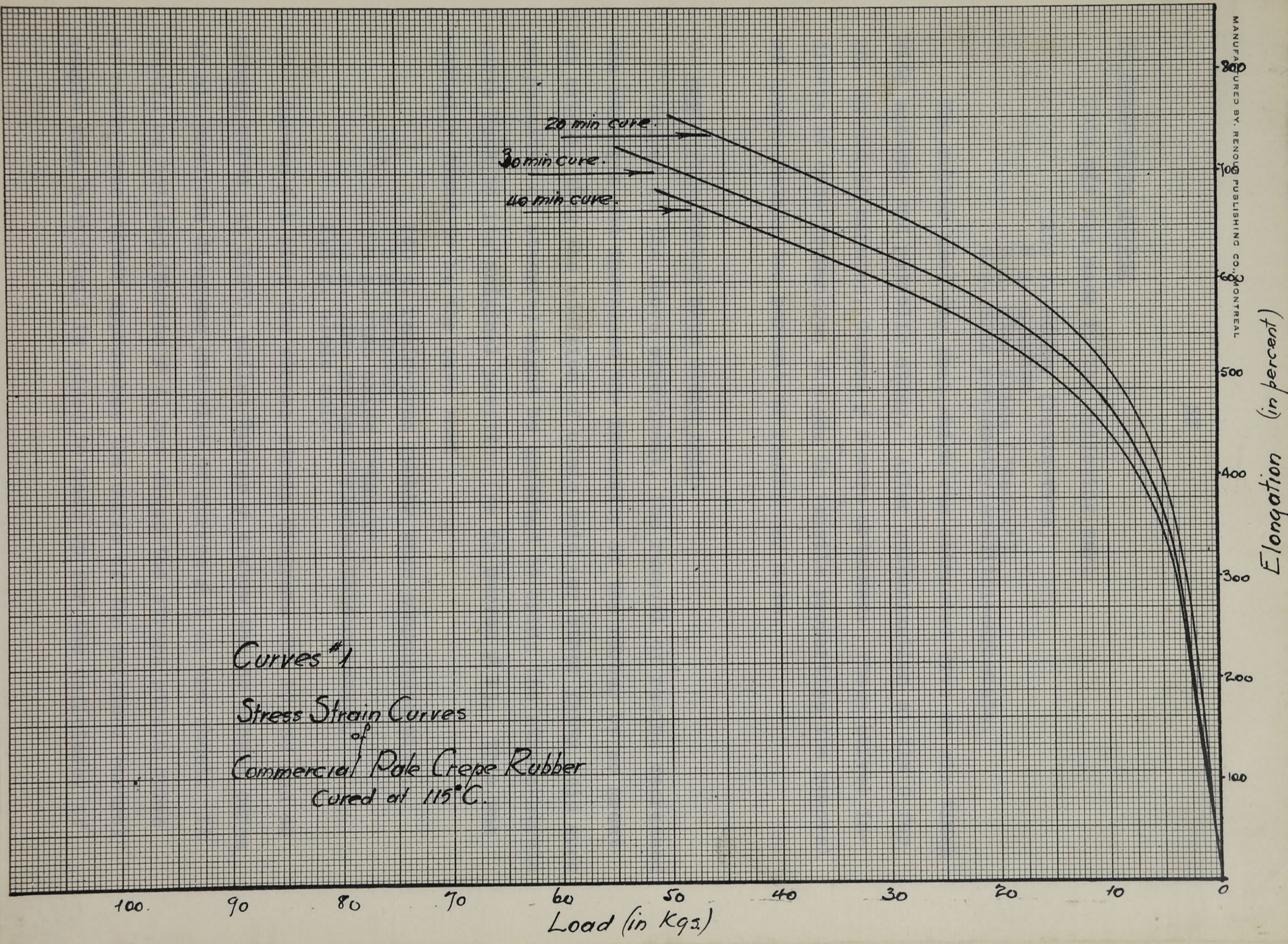
[1] G. S. Whitby Trans. Institution Rubber Ind. <u>1</u> 12. 1925.



Curves #1

Stress Strain Curves
of
Commercial Pale Crepe Rubber
Cured at 115°C.

B. Resin-Free Rubber

This mix was made in the following way:

100 g. Rubber (resin-free)
5 g. Sulphur
5 g. Zinc oxide ("kadox")
.5 g. Zinc pentamethylenedithiocarbamate.

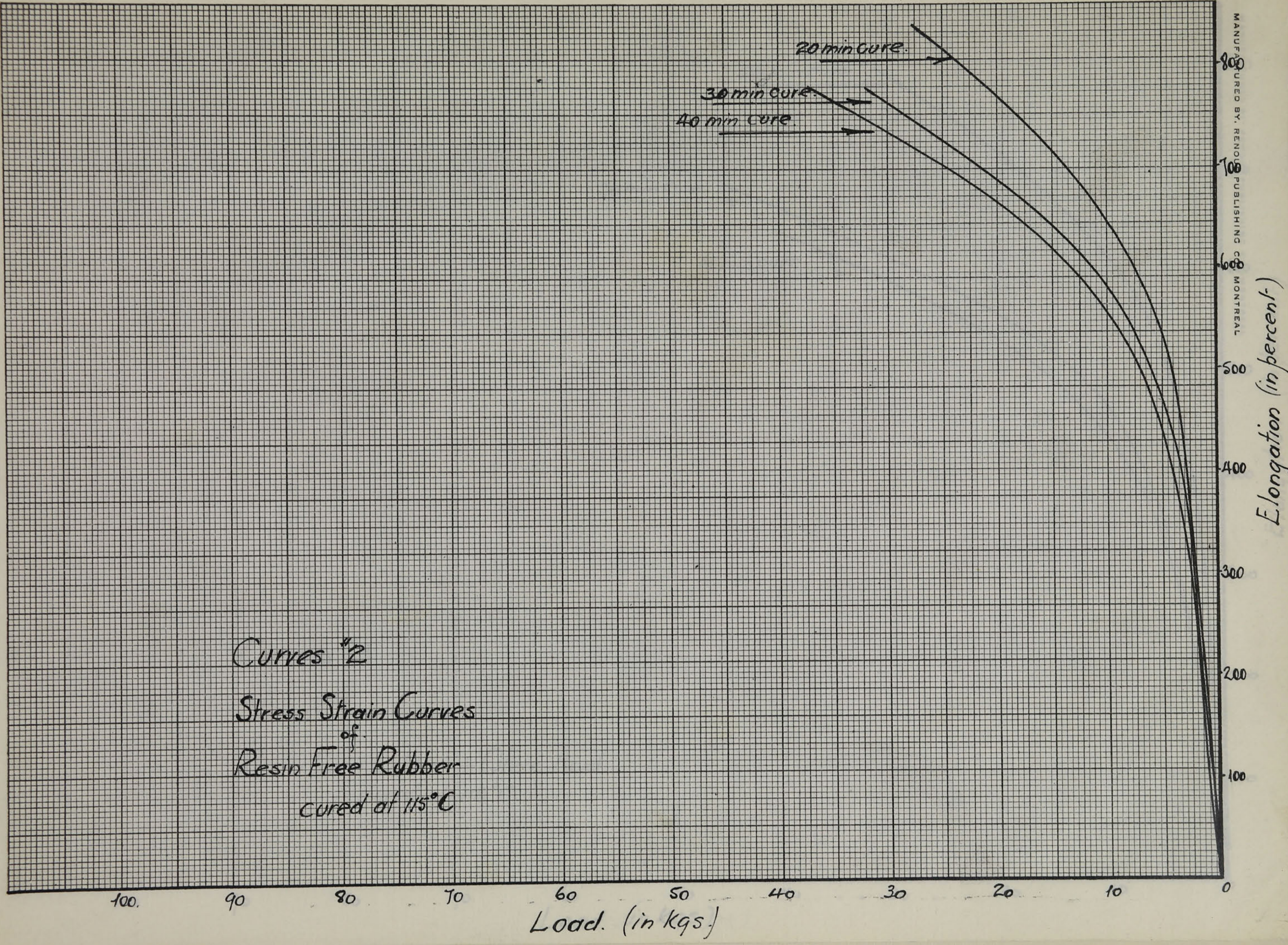
The rubber used was that which was extracted five or six times with acetone and petrolic ether. After vulcanization at 115°C for 20, 30 and 40 minutes, Curves # 2 were obtained. These curves indicate at once tremendous changes in tensile properties the removal of approximately two percent of resins may make.

C. Resin-Free Rubber plus Oleic Acid.

If, as in the above experiment, the removal of resins decreased the strength and increased the intensity of the rubber by so great an extent, then the addition of oleic acid (or other fatty acid such as palmetic or stearic) might be expected to bring the stress-strain curve back to its original position (as in Curves # 1). This was actually found to be the case when

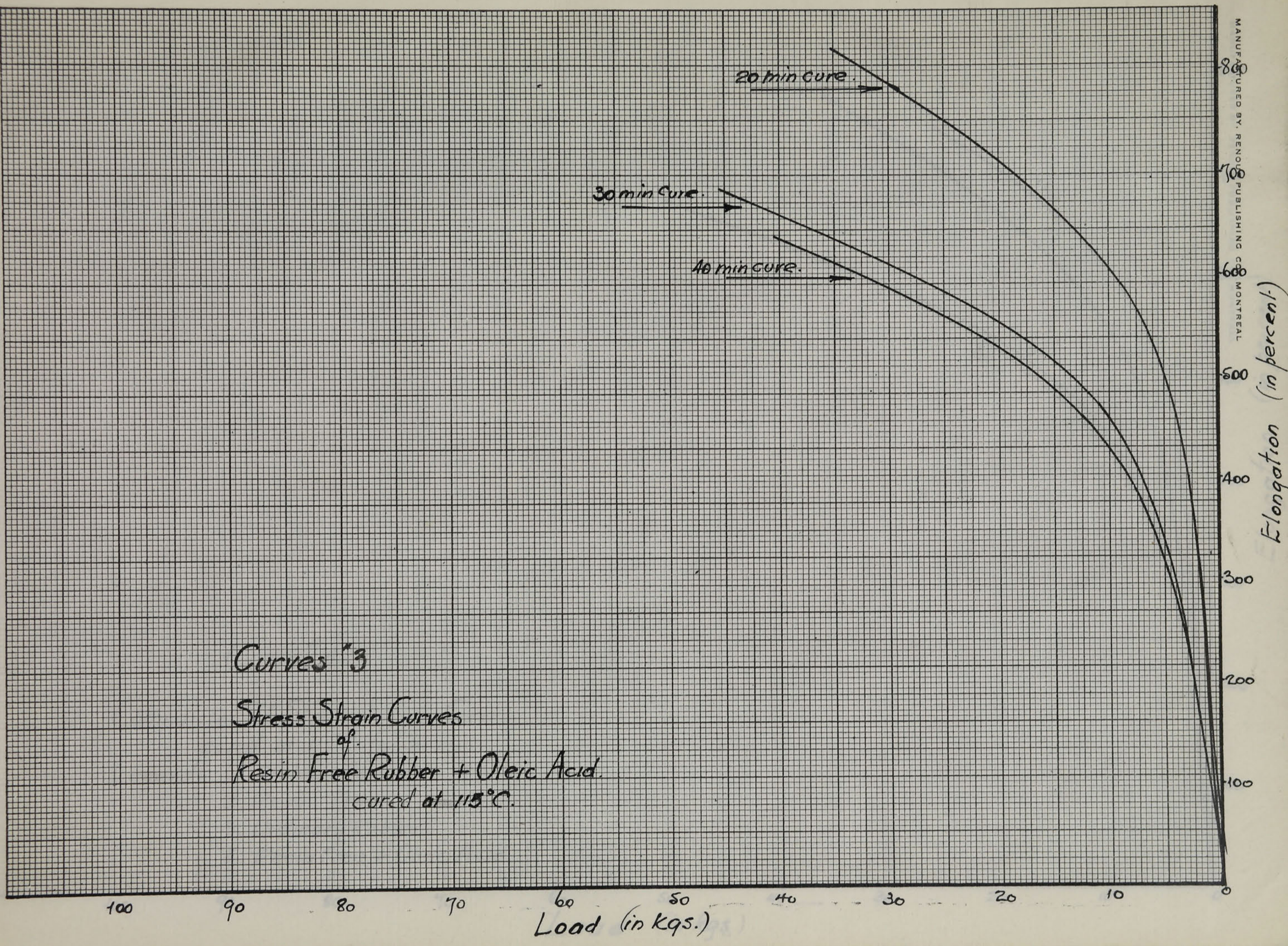
100 g. resin-free rubber were compounded with,
5 g. sulphur,
5 g. zinc oxide ("kadox"),
.5 g. zinc pentamethylenedithiocarbamate,
1.5 g. oleic acid.

Curves # 3 give the stress-strain diagrams for 20, 30 and 40 minute cures at 115°C, whilst Curves # 4 show the 30 minute cures of all previous diagrams and also of curves # 5 on one sheet. It should be noticed (Curves # 4) how close the stress strain curve of resin free rubber approaches the curve of the original control sample when oleic acid is added to make up for the deficiency of



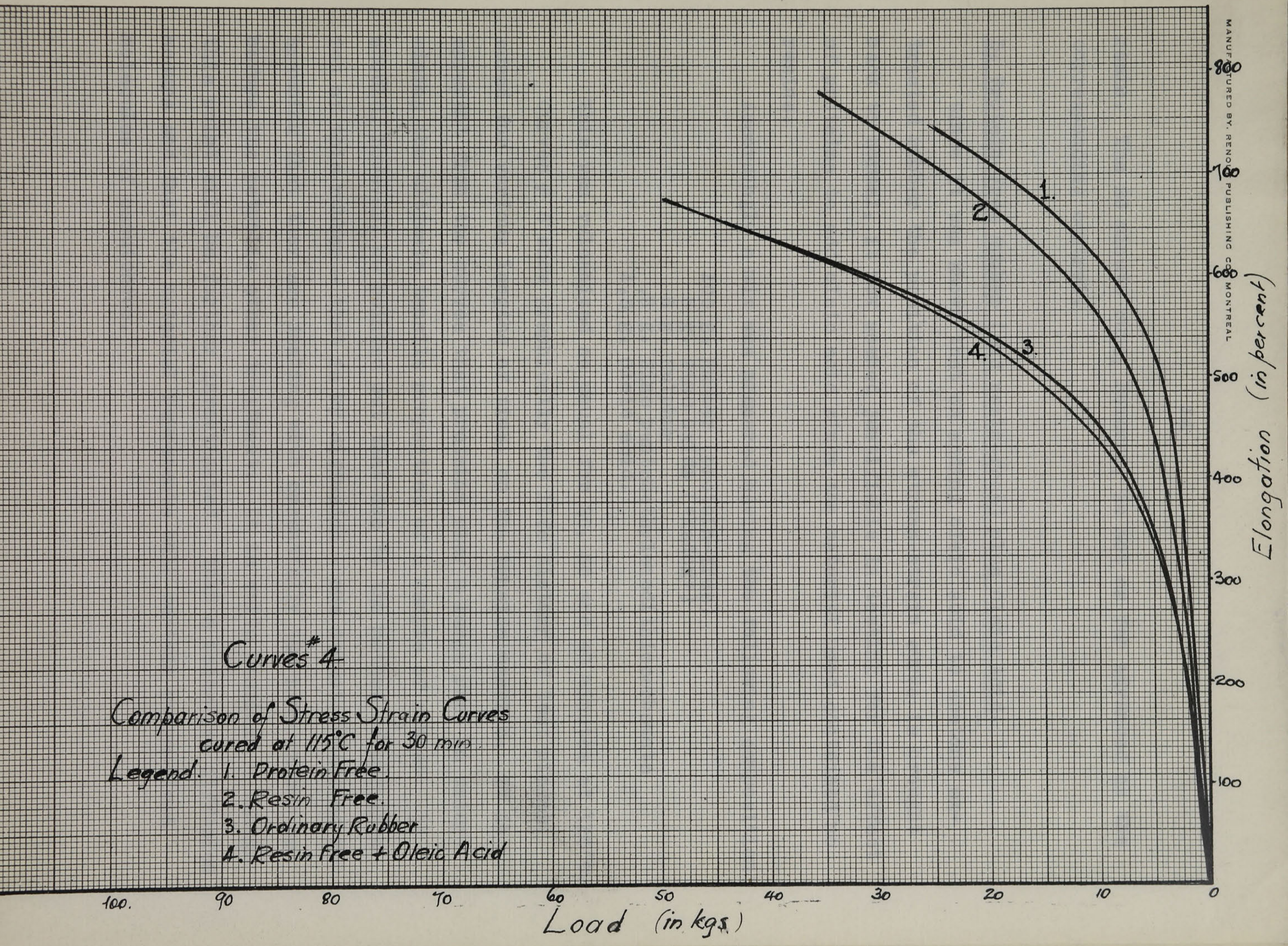
Curves #2

Stress Strain Curves
of
Resin Free Rubber
cured at 115°C



Curves #3

Stress Strain Curves
of
Resin Free Rubber + Oleic Acid.
cured at 115°C.



Curves # 4.

Comparison of Stress Strain Curves
cured at 115°C for 30 min.

Legend.
1. Protein Free.
2. Resin Free.
3. Ordinary Rubber
4. Resin free + Oleic Acid

resin. The 20 minute cure, however, is not as far advanced as the corresponding control.

D. Protein-Free Rubber (and resin-free) plus Oleic Acid.

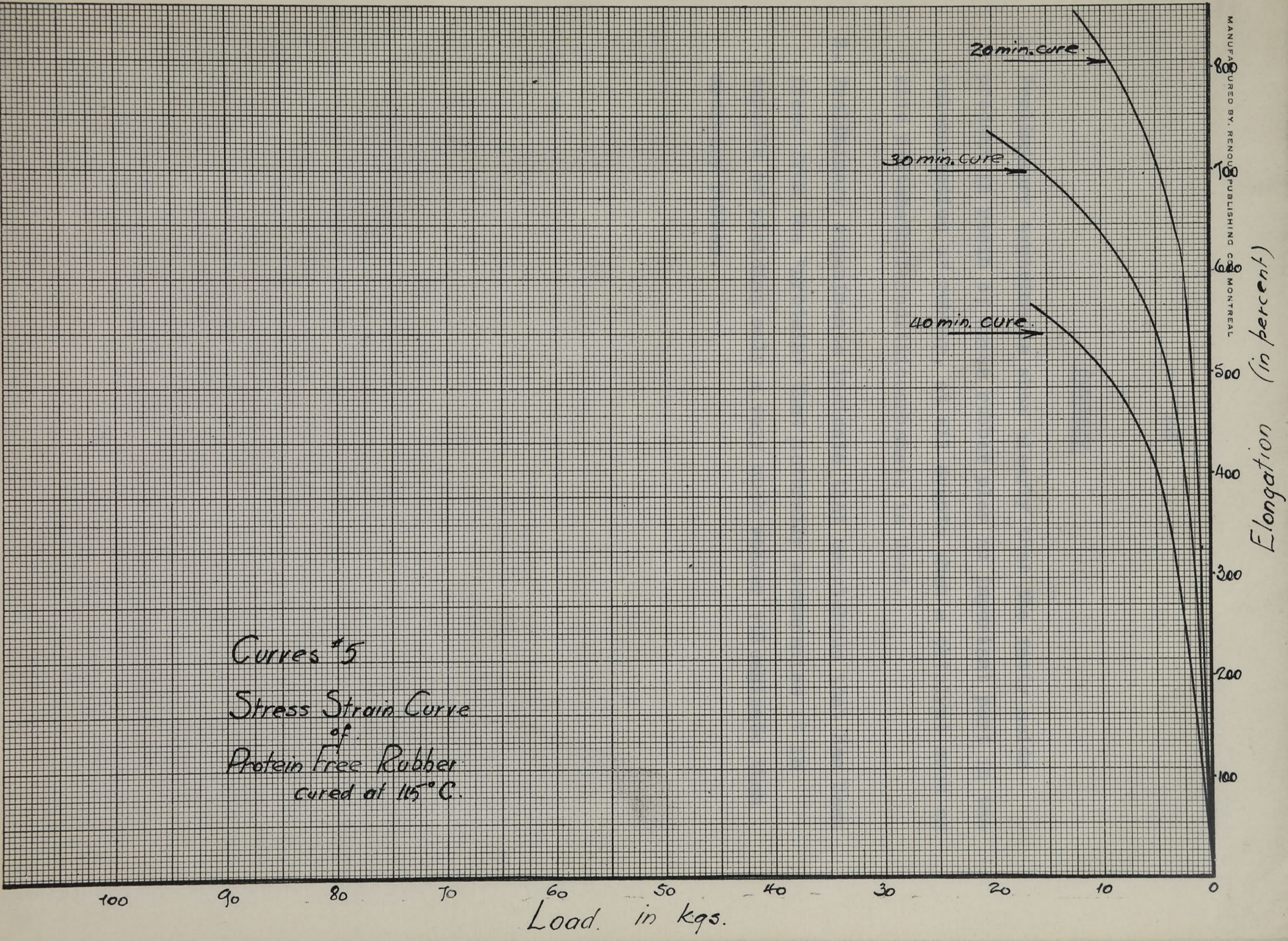
Since it was shown that on adding oleic acid to acetone extracted rubber the position of the stress-strain curve is brought back to normal, it now seemed justifiable in testing for the effect of proteins to add oleic acid since the material used contained no resins.

Accordingly a mix was prepared having the following composition:

100 g.	Rubber (protein-free)
5 g.	Zinc oxide ("kadox")
5 g.	Sulphur
.5 g.	Zinc pentamethylenedithiocarbamate
1.5 g.	Oleic acid.

This was vulcanized as usual for 20, 30 and 40 minutes at 115°C.

Curves # 5 show graphically the life history of test pieces, cured for various lengths of time, on the tension machine. It is apparent from the curves that proteins play a large part in determining the ultimate tensile properties of a sample of rubber. It should, however, be pointed out that due to the method of preparation of this rubber - that is by diffusion - one is not justified in assuming that they are dealing with essentially the same rubber as before the petrolic ether treatment. It is quite possible - though this point will be further investigated - that a selective diffusion occurs and that the material represents only certain polymerized molecules of caoutchouc.



Curves #5

Stress Strain Curve of Protein Free Rubber cured at 115° C.

Summary

1. Preliminary experiments show clearly that the fatty acids present in resin of Hevea rubber play an important part in the vulcanization of rubber, at all events when a catalyst such as zinc pentamethylenedithiocarbamate is used.

2. Preliminary experiments indicate that caoutchouc that has been freed from the "protein" that naturally accompanies it is capable of yielding only a very much weaker vulcanizate than ordinary rubber.