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ON CERTAIN
UNSATURATED SUBSTANCES
ESPECIALLY FATTY OILS

THE ACTION OF SULPHUR AND SULPHUR HALIDES ON CERTAIN UNSATURATED SUBSTANCES, ESPECIALLY FATTY OILS.

THESIS

by

DAVID S. PASTERNACK,

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INTRODUCTION

Although the thickening of oils with and without the presence of air and catalysts has occupied the attention of chemists for many years owing to its recognized industrial importance, the sulphurization of oils has, on the other hand, been practically neglected. Since sulphur and oxygen are very similar elements, especially as regards the compounds they form, it appeared that the changes taking place during the sulphurization process would be analogous to those in the oxidation process, and quite recently (1) this was shown to be the case. The sulphurization process has the advantage in that it takes place much more quickly, the setting-point is more sharply defined, side-reactions occur to a smaller extent owing to the lower temperatures used, and the experimental conditions can be standardized more easily as a definite quantity of sulphur can be added all at once whereas oxygen or air can be introduced into the oil only gradually.

The object of the present investigation was to study the effect of accelerators in the sulphurization of oils as it seemed likely to throw more light on the mechanism of rubber vulcanization. Vegetable drying oils were considered a satisfactory starting-point as they combine with sulphur at comparatively low temperatures yielding a substance of rubber-like consistency.

HISTORICAL

Vegetable oils are mixed glycerides of organic acids, both saturated and unsaturated, and are usually classified according to their power of setting to a solid, without loss in weight, when exposed to the air in thin films.

Three main groups are recognized: non-drying oils, e.g. olive oil; semi-drying oils, e.g. corn oil; and drying oils, e.g. linseed and china wood oils. The drying properties of the last group were considered due to the presence of a considerable quantity of the highly unsaturated fatty acids, namely, linolic and linolenic acids, but it has recently been shown that the alcohol in combination with the fatty acids is very important as the methyl and ethyl esters will not set. The drying of an oil is due to its combination with oxygen, but the drying is possible in any other atmosphere which allows of combination with the gaseous medium and coagulation of the product.

Although the drying properties of oils have been found to depend upon their content of unsaturated acids, and hence upon their iodine number, the latter is not always a criterion of the rapidity of setting. China wood oil with an iodine number of 160-170 dries more quickly than linseed oil with an iodine number of 175-200. The iodine number does serve to distinguish between the three main classes of vegetable oils as non-drying oils have an iodine number of 80-100, semi-drying oils from 100-120, and drying oils over 120.

Owing to the complex nature of oils and the fact that the composition depends on the maturity of the seed and the place where it is obtained, only a few investigators have attempted to determine their composition. Their work has served to indicate the constitution of the unsaturated acids which are found. Of the numerous possible isomers of oleic acid depending upon the position of the double bond, the one generally considered as being present in, say, linseed oil is :

$$CH_3.(CH_2)_7.\underset{10}{CH}=\underset{9}{CH}.(CH_2)_7.COOH$$

Linoleic acid is assigned the formula:

$$CH_3.(CH_2)_4.\underset{13}{CH}=\underset{12}{CH}.CH_2.\underset{10}{CH}=\underset{9}{CH}.(CH_2)_7.COOH \quad (2)$$

The formula given to linolenic acid by Erdmann, Bedford and Raspe (3) is:

$$CH_3.CH_2.\underset{16}{CH}=\underset{15}{CH}.CH_2.\underset{13}{CH}=\underset{12}{CH}.CH_2.\underset{10}{CH}=\underset{9}{CH}.(CH_2)_7.COOH.$$

Linoleic acid absorbs four atoms of oxygen from the air when exposed as a thin film, and is converted into a solid resinous substance (a linoxyn) which is insoluble in ether (4) . No volatile products are formed. Coffey (5) showed that linolenic acid absorbs nine atoms of oxygen to give a peroxide linoxyn and volatile products consisting of carbon dioxide and acids (acetic acid). His scheme for the oxidation of linolenic acid is:

$$C_{18}H_{30}O_2 + 9O \rightarrow \text{linoxyn} + CO_2 + \underset{\text{(volatile acids)}}{CH_3COOH} + H_2O.$$

When the oxidation of linolenic acid was carried out with hydrogen peroxide or perbenzoic acid, Bauer and Kutscher (6) found that the amount of oxygen taken up varies with the experimental conditions. With hydrogen peroxide only part of the double bonds disappear, the iodine number becoming 91.5 at room temperature and 55.9 at 100°C. In both cases molecular weight determinations in benzene indicate that a bimolecular compound has formed. Perbenzoic acid causes the linolenic acid to become saturated, and the iodine number falls to 3.45. The ethyl ester of linolenic acid does not react with hydrogen peroxide, and although perbenzoic acid does oxidise it the product formed is monomolecular. Oleic acid and its ethyl ester are not acted on by hydrogen peroxide, but perbenzoic acid causes the acid to absorb two atoms of oxygen per molecule with increase in molecular weight, whereas the ethyl ester absorbs only one atom of oxygen and remains a simple molecule .

Linseed oil is considered to consist of mixed glycerides of linolenic, linolic and oleic acids, together with glycerides of the saturated acids, palmitic, stearic, and possibly small quantities of myristic and arachidic. The following mixed triglycerides have been identified and isolated in the form of bromo-derivatives:-

(a) dilinolenylmonolinolyl glyceride,

$$C_3H_5(OL_2)_2\ OL_1 \qquad (L_2=\text{linolenyl}, L_1=\text{linolyl})$$

(b) 25 per cent. of the trilinoleic glyceride or an oleic-linoleic-linolenic glyceride,

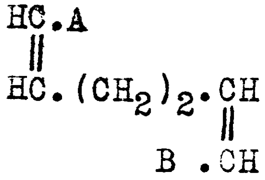
(c) dioleopalmitin (0.6 per cent.) (7)

Very recently Eibner, Widenmayer, and Schild (8) have isolated dilinoleno-mono-olein. They also consider that dilinoleic-monolinolenic glyceride is present. They believe that (a) above is the chief drying constituent of linseed oil.

China wood oil, on the other hand, contains glycerides of α- and β- elaeostearic acids together with small quantities of olein (10 - 15 per cent.) It is almost a simple one-acid glyceride as compared with the mixed glycerides of other drying oils. Elaeostearic acid (also called margaric acid) was considered to be isomeric with linoleic acid and given the formula:

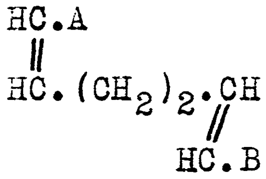
$$CH_3.(CH_2)_3.\underset{14}{CH}=\underset{13}{CH}.(CH_2)_2.\underset{10}{CH}=\underset{9}{CH}.(CH_2)_7.COOH.$$

Now, however, Boeseken and Ravenswaay (9) believe that the elaeostearic acids have three ethenoid linkages and are stereoisomeric with the linolenic acids, and in this way they account for the great reactivity of china wood oil. The same authors have shown that the α- and β- elaeostearic acids are themselves stereoisomeric by determining their molecular reactivity. By analogy with oleic and elaidic acids they are considered to be bi-cis and cis-trans respectively.



$$\begin{array}{l} \mathrm{HC.A} \\ \;\| \\ \mathrm{HC.(CH_2)_2.CH} \\ \qquad\qquad\quad\;\, \| \\ \qquad\qquad\;\; \mathrm{B\ .CH} \end{array}$$

Bi-cis form



$$\begin{array}{l} \mathrm{HC.A} \\ \;\| \\ \mathrm{HC.(CH_2)_2.CH} \\ \qquad\qquad\quad\;\, / \! / \\ \qquad\qquad\;\; \mathrm{HC.B} \end{array}$$

Cis-trans form

From spectographical observation of typical acids and comparison of their absorption curves Manecke and Volbert (10) decide in favour of the opinion that elaeostearic acid has three double bonds, but have no definite information as to their conjugation.

The α- acid can be converted into the β- form by the action of nitrous acid or by iodine and sulphur (11)

Drying at Room Temperature

On exposure to the air in thin films at room temperature raw linseed oil sets within 3-7 days to a smooth glossy film. This relatively hard, tough, elastic substance is known as linoxyn. The chief chemical changes which are apparent are: absorption of oxygen, evolution of volatile decomposition products, drop in the iodine number, increase in the amount of combined oxidized acids, and increase in density. These changes depend upon the absorption of oxygen, and it is found that there is a distinct induction period.

The absolute changes that take place vary with the conditions. Genthe (12) noticed that linseed oil which absorbed 22.6 per cent of oxygen under ordinary conditions would absorb

25.8 per cent. when exposed to the light of a mercury vapor lamp. At 95°C. the gain in weight in air corresponded to an absorption of 26.8 per cent. whereas in an atmosphere of oxygen it was 34.7 per cent. For a rise of ten degrees a reduction by a half in the time of drying was obtained. Also the final hardening of the film took place more rapidly in dry air than in an atmosphere saturated with moisture owing to the fact that in the presence of moisture there is a second great rise in the weight time curve (13). This second maximum is often greater than the first, whereas in the presence of dry air it is usually slight or even entirely lacking.

Effect of Driers

As has been mentioned before, there is an induction period in the absorption of oxygen during the drying of an oil. Driers were found to remove this induction period, and also to affect the percentage of oxygen absorbed and the final behaviour of the solid film. When driers are used the oxidation curves do not run parallel to that for linseed oil alone. Ingalls obtained the following results with linseed oil films (0.001-0.003 inches thick) containing 2 per cent. of resinates of the following metals.

Linseed oil containing	Mn	Pb	Zn	Ca	Cu	Fe	Al	Cr	Linseed oil alone
Drying time (hours)	12	26	30	32	46	60	85	95	121
Percentage	17.4	9.4	6.5	6.0	4.9	4.1	2.8	2.0	0.93

Marked variations are observed in the specific action of metallic driers. Manganese and cobalt are looked upon as producing superficial oxidation, whereas lead driers, although much slower in their action, favour the production of a more uniformly oxidized film. Very small amounts of manganese and cobalt (up to 0.2 per cent.) produce almost maximum acceleration, whereas in the case of lead and others a much larger quantity of drier is necessary. Combinations of driers, e.g. lead-manganese, are better driers than the individual metals. The activity of lead driers is less sensitive to temperature variations, whereas manganese driers are peculiarly sensitive (14).

Recently it has been found that small quantities of solid substances, which can have little or no chemical effect on the properties of the film, nevertheless exert a strong influence on the setting of the oils even in the presence of metallic driers. Ortho-amidobenzoic acid and salicylic acid are such substances. They produce a softening action, and also accelerate the rate of absorption of oxygen with consequent reduction in the time of setting. This is especially noticeable in the case of tung oil, where the hardening is very slow indeed.

Rogers and Taylor (15) have found that substance such as hydroquinone, beta-naphthol, and diphenylamine act as inhibitors in the oxidation of linseed oil, and that they are more effective at lower temperatures just as is the case with driers. They believe that the inhibitor does not act solely by suppression of the catalyst but that both may exert their influence independently.

The catalytic action of the metallic driers is considered by Ingle (16) to be due to the formation of an intermediate substance between the triglyceride and the drier, and this then aids in the activation of the oil or the oxygen or both with formation of a peroxide of the oil. Carbon dioxide is evolved from linseed oil whether driers are present or not, but no hydrogen peroxide is formed when driers are employed (17).

Rhodes and van Wirt (18) made a systematic study of the influence of pigments in the case of linseed oil. Their action was found to be varied, some accelerating the setting and others retarding it. In most instances they affected the quantity of oxygen absorbed and volatile products formed (generally decreasing them), and sometimes reduced the period of induction. As a whole the pigments were not found to act like true driers.

From an exhaustive investigation of the oxidized film Ellis (19) confirmed Mulder's (20) work as regards the composition of the oxidized film of linseed oil, and states that the formula corresponds to a mixed glyceride containing two molecules of linolic acid and one molecule of linolenic acid. This composition does not correspond with that of Eibner obtained by direct analysis of the oil.

The researches on the oxidation of linseed oil indicate that the initially formed peroxide is not a permanent substance.

Wolff, Borries, and Morrell (21) consider that it gives rise to monoxides which polymerise. Rochs, and Salway (22) believe that decomposition of the monoxide occurs with formation of aldehydes, acids, and carbon dioxide, and that polymerisation of the aldehydes takes place.

China wood oil, often called tung oil, dries in from one to three days, but the film, unlike that of linseed oil, is dull and frosted in appearance. It sets in about half the time required for the weight of the oil to rise to a maximum, whereas in the case of linseed oil setting occurs when the weight of the oil has reached a maximum. The acid number increases during the drying, but not to the same extent as in linseed oil. China wood oil added to other less rapidly drying oils decreases the time of setting of thin films of the oil.

Boiled and Blown Oils

Similar changes occur during the commercial processes of boiling and blowing oils with the addition of driers, air being present when boiling . In both cases considerable oxidation occurs, and thin films readily set in a much shorter time than is the case with raw linseed oil. Blown china wood oil is not prepared commercially because of the danger of its setting during its preparation.

Another important commercial process is that of heating the oils to a high temperature in the absence of air. The product is simply a thickened oil and is called polymerized oil. In an experiment performed by Slansky, linseed oil set after heating in a carbon dioxide atmosphere at a temperature of 280-300°C. for 115 hours. The iodine number dropped from 174.6 to 105.5, and the viscosity increased steadily until within an hour of setting. At the setting-point the viscosity rose suddenly and the material, instead of being completely soluble in ordinary solvents, became partly insoluble.

Oils are also thickened at comparatively low temperature, e.g. 80°C., by exposing the oils to ultraviolet light and blowing air through them.

Theories

In order to explain the phenomenon of the thickening and gelling of oils, many theories have been put forth, some chemical and some physical.

Kronstein (23) distinguishes in general between two kinds of polymerisation which he terms euthomorphic and mesomorphic. In euthomorphic polymerisation a solid polymerised body is formed in a non-polymerised medium and immediately precipitates out. In mesomorphic polymerisation a polymerised body is formed which is at first soluble in the non-polymerised medium, but which, when it reaches a certain percentage concentration, suddenly combines with the medium to form a solid mass. If the heating is interrupted before gelatinisation occurs a solid body may be isolated which is a polymer of the original substance. This polymer cannot be isolated from the gel finally formed, and Kronstein therefore considers it an intermediate product. This kind of polymerisation is very wide-spread.

He points out that China wood oil, on heating either in contact with or in the absence of air, exhibits the series of changes characteristic of mesomorphic polymerisation in that it thickens and then changes to the gelatinous state. All the other oils thicken in the absence of air and, if not heated too long, do not set. Hence he considers that China wood oil is either a polymerisable body or a gelatinisable mixture. Hence the other oils are considered non-gelatinisable mixtures of polymerisable and non-polymerisable glyceryl esters, and therefore he concludes that if their percentage content of polymerisable bodies was increased they would also set.

In order to prove this Kronstein made a vacuum distillation of numerous oils. He found that distillation began about 300°C. Suddenly it stopped, and the oil in the distilling flask foamed and became more viscous. On cooling the mass was found to be gelatinous . The percentage that distilled over he called the distillation number of the oil, and found that the distillation number varied between 0 - 25% for drying oils, 25% - 43% for semi-drying oils, and around 50% for non-drying oils.

By carrying out the distillation to within about 5% of the distillation number he obtained a thick oil, which, on heating in a sealed tube, gelatinised similarly to China wood oil.

Since the second reaction, namely that between the intermediate product and the unchanged monomer, is so rapid, Wolff (24) and others have criticised the theory on the ground that it is difficult to understand why the second reaction does not commence as soon as some of the intermediate product has formed. He points out that it is only when the second stage is slow that the first part of a two-stage reaction can proceed alone. Moreover, Kronstein stated that in a typical mesomorphic polymerisation the intermediate product combines with the unchanged monomer to form a solid mass, but several workers have found it possible, by prolonged extraction, to separate a considerable quantity of oily material from the end-product. Wolff obtained as much as 80% from a solidified China wood oil (25).

Turning now to the drying process, that is, the setting of oils through the action of oxygen, Slansky (26) says that the important point to notice is the coagulation of oxidised glycerides in non-oxidised or perhaps non-oxidisable glycerides. This he considers to be a colloidal change as will be seen from the following table in the case of blown linseed oil:

No.of sample	Time of heating	Consistency of the oil	Iodine No.	% Oxy-acids	Solubility in ether
1	2 hours	somewhat viscous	145	9	Soluble
2	4	viscous	123	20	"
3	9	"	106	33	"
4	12	very viscous	97	35	"
5	15.5	"	88	39	"
6	18	solid	80	40	partially soluble

The viscosity is seen to increase with progressive oxidation. Sample No.5 with 39% of oxy-acids is a liquid still soluble in all the ordinary fat solvents (ether, chloroform), whereas No.6 with 40% of oxy-acids is a solid elastic body that is only partially soluble in the usual solvents. Hence only a small change in the degree of oxidation results in a sudden change in the state of aggregation and in the solubility of the oxidised oils. Obviously linoxyn owes its main characteristics — solidity, elasticity, and insolubility in organic solvents — not to the oxidation of the linseed oil but to the coagulation of the oxidised glycerides, as sample No.5 is a sol and No.6 a gel. Consequently the drying process includes two processes; firstly, oxidation of the glycerides, and secondly, coagulation of the oxidised glycerides.

Further, Slansky states that of two oils, each oxidised to the same extent, one can be a fluid and the other a solid. Hence the coagulation point depends upon other factors besides the proportion of oxidised glycerides. Therefore the oxygen absorption can give no conclusive indication of the drying power of a sample of linseed oil. The molecular weight of linoxyn is not the same as that of the oxidised glycerides since linoxyn is formed by the condensation of two or more molecules of the oxidised glyceride.

By heating linseed oil at 280-300°C. in an atmosphere of carbon dioxide Slansky found that the polymerisation process proceeds similarly to the drying process.

No. of sample	Time of heating	Iodine No.	Consistency	Solubility in Org. solvents
Raw oil	0	174.6	fluid	soluble
1	16 hrs.	153.9	"	"
2	32	127.3	"	"
3	50	125.8	"	""
4	114	105.5	"	"
5	115	105.9	solid	partially soluble

Between numbers 4 and 5 the polymerised oil coagulated, and merely to this is due its insolubility in ether and its solid state of aggregation.

Many investigators noticed that the final product of the thickening of linseed oil is insoluble in light petroleum, whereas the intermediate product is soluble in light petroleum but insoluble in acetone. Similar intermediate products were obtained from poppyseed and tung oils, but in the case of poppyseed oil the temperature must be over 290°C. Olive oil does not give this insoluble product. Morrell (27) observed that a fall in the iodine number is essentially a function of the temperature, and so assumed that at each temperature a definite change in the linseed oil occurred. Molecular weight measurements in benzene indicated that the acetone-insoluble material of the thickened linseed oil was at least a dimeride, whereas the acetone-soluble part was practically all unpolymerised oil. The iodine value of the two parts was practically identical indicating that the changes taking place in the oil affects every molecule. He found that the iodine values of linseed or tung oils are practically unchanged even when the oil is left in contact with the iodine solution for hours or even days, but the iodine values of the thickened components may vary by thirty to forty units under the same conditions. This variation he explains as due to a slow disruption of the polymerised molecules.

From a consideration of the solubilites of the barium and lead salts of the acids derived from each fraction, Morrell concluded that all traces of linolenic and linolic acids had disappeared.

On further heating of the acetone-soluble portion of linseed oil it changed into an acetone-soluble and acetone-insoluble fraction similar to the one already described. The molecular weight of this insoluble fraction represented four and five molecules joined together.

Later (28) Morrell decides that the use of benzene in the determination of molecular weights is unreliable since association of the fatty acids and combination of the esters with the solvent will occur. He considers that acetic acid or stearic acid give better results.

In 1915 Schumann (29) carried out a series of experiments on China wood oil, and concluded that the polymerisation was mesomorphic. Investigating the action of oxygen on the time of formation of a gel he observed that China wood oil solidified in 2-1/2 hours when blown at 150°C.and in less than an hour when blown at 200°C. Heated in an open dish but not blown it did not gelatinise for thirty hours. Further experiments indicated that it was the oxidation products,and not the oxygen itself,which caused the increased rate of polymerisation. He considered that, upon heating at sufficiently high temperature,two elaeomargaric acid triglyceride molecules united through dissolution of one-half of their double bonds. The rate of formation of this intermediate product depends upon the temperature as well as upon the presence of catalysers. Under favorable conditions this intermediate product forms molecular complexes that constitute the gel, the colloidal state of which is apparently the main cause of its insolubility. The formation of these complexes is largely dependent upon the concentration, and is influenced by the presence of certain substances acting as retarding or accelerating catalysts. In the presence of a small quantity of decomposition products or in the presence of a diluting solvent we may have complete polymerisation of the elaeomargaric acid to the dimolecular intermediate product without gel formation taking place.

The absence of gelatinisation in the superheated product upon heating afterwards to polymerising temperatures must be due to the presence of the decomposition products formed during the superheating because the formation of the intermediate product was complete. On the addition of 25% raw tung oil to a superheated oil the mass readily gelatinised at polymerising temperatures. Therefore he claims it is apparent that a minimum concentration of decomposition products are required to prevent gel formation.

Marcusson (30) put forth a hypothesis to explain the fact that blown oil, in spite of the polymerisation that has occurred, has no higher molecular weight than unblown oil. He states that the polymerisation of fatty oils can occur in two ways. Two triglyceride molecules can unite because the unsaturated fatty acids of one molecule link up with those of a second molecule with consequent disappearance of the double bond. Also the reaction can take place intramolecularly if the fatty acids of one and the same glyceride combine together either directly or by the addition of oxygen. The polymerisation which occurs during the blowing of fatty oils proceeds in the latter manner, and accordingly the molecular weight of the resulting product is not increased. Sometimes the molecular weights are lower than that of the original oil, but this can be explained by a decomposition of high molecular weight fatty acids under the action of oxygen as in blown oils there are considerable quantities of water-soluble and volatile acids present.

Bimolecular formation occurs, on the other hand, during the heating of fatty oils without the presence of air as it is technically carried out, for example, in the production of lithographic varnish. In that case the polymerisation increases with the duration and the degree of heating.

In the case of China wood oil bimolecular polymerisation occurs with exceptional ease. The polymerised product at first remains in solution; then separates out to form an insoluble portion. A China wood oil which had been heated by Marcusson to 200-250°C. until gelation was found to contain 40% of ether-soluble material. This ether-soluble material consisted of 12% acetone-insoluble material which was a thick, oily, viscous mass and 88% of acetone-soluble material not much more viscous than the original oil. Judging by its iodine number (89) and its molecular weight (1670) the thick oil consisted of a bimolecular elaeostearic triglyceride,whereas the acetone-soluble product was a mixture of unchanged oil with a small quantity of thick oil, the molecular weight of the mixture being 985. By warming, and even by standing in the air, the thick oil,which was still soluble in benzene, ether, and chloroform,changed over into an insoluble solid mass.

Consequently Marcusson concluded that in solidified China wood oil there are,besides oxidation products and anhydrides, three components: unchanged oil, oily polymerisation products, and solid polymerisation products, the proportions of which are variable and depend upon the conditions of heating. The oily and solid polymerisation products are not chemically different but are to one another as a sol is to a gel.

In the case of linseed oil bimolecular products are also formed, but they have a tendency to remain in the sol stage because, during the heating process, which is carried out at a higher temperature than it is for China wood oil, the linseed oil splits off free fatty acids which oppose gel formation. By removing the free acids as soon as formed by heating in vacuo or by blowing through a rapid stream of an indifferent gas, gel formation sets in, according to Schapringer and Krumbhaar, just as in the case of China wood oil.

Wolff (24) determined the drop in bromine number (which corresponds to the iodine number) upon heat treatment, and the increase in viscosity. These should be proportional to one another if the bodying is due merely to polymerisation, that is, to the formation of a dimolecular triglyceride. The bromine number was found to drop rapidly in a straight line, then more slowly, and finally remain constant. As long as the bromine number was dropping the viscosity increased only slightly, and then rose with increasing rapidity. The rapid rise occurs when the bromine number (and incidentally the refractive index) has reached its minimum value. From that point the shape of the viscosity curve is that for a typical colloid. Thus it follows that the colloid reaction proceeds when the chemical change has already occurred, and it is the former which causes gel formation.

The same author also investigated the extent to which polymerisation actually occurs. He points out that the observed drop in the bromine number in the case of China wood oil corresponds to the formation of about 50% of a polymerisation product on the assumption that only one of the two double bonds in each acid radicle is affected. The actual increase in the molecular weight was so much larger than expected that he suspected they were in part due to association of the material taking place in the solvent,as the association weight of a compound varies with the conditions used.

To verify the above point he determined the molecular weight by Rast's camphor method (31). He found that the molecular weights of the thickened oils and of the fatty acids derived from them were no greater than those of the original oils and of the corresponding acids, his work covering China wood , linseed, and soya-bean oils.

Wolff therefore concluded that polymerisation can occur only to a very small extent in the bodying of an oil, and in no case can this amount of polymerisation account for the considerable diminution in the bromine number (or iodine number) which actually occurs. He suggests that the change need not necessarily be a chemical one as an aggregation of oil molecules might be so arranged as to retard the addition of bromine.

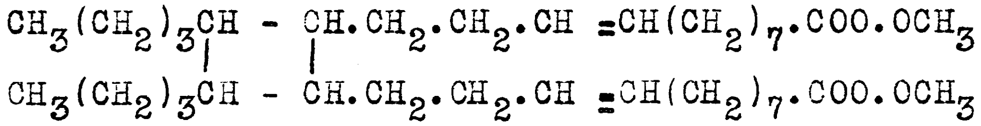
In reply Marcusson (32) pointed out that his molecular weight determinations of the liberated acids from blown oils were carried out in acetic acid with the purpose of avoiding association. He also stated that the molecular weights of the acids from a China wood oil and a linseed oil gel were determined in camphor as well as in acetic acid, and in both cases they were found to represent a dimeride.

Wolff (33) then suggested that too high a concentration had been used by Marcusson in his molecular weight determinations, but the latter (34) then showed that the concentrations used by him were no greater than those used by Wolff, and that moreover his results using two different methods agree and thus prove that the liberated acids are bimolecular.

Later work by Wolff (35) showed that linseed oil varnishes will dry slowly in an atmosphere containing so little oxygen that the drying process must be essentially of the colloid type, and is possibly independent of the oxidation reaction. Also (36) the gelatinising of China wood oil by a few drops of ferric chloride solution, hydrochloride acid, or sulphur dioxide changes the iodine number very little when compared with the considerable decrease of the iodine number by heat.

Schmidt (37) upholds Wolff's coagulation theory by finding that in the absence of moisture tung oil dries comparatively slowly, and believes that the commonly observed drying consists of a colloidal coagulation with water as the flocculating medium. Bauer and Hügel (38) consider colloidal changes to function in the drying of perilla oil and Stadnikoff (39) in that of sunflower oil.

Nagel and Grüss (40) also incline partially to the view of Wolff who regards the gelatinisation process as one of aggregation as has been shown to be the case for shellac (41). Using the methyl ester of elaeostearic acid, which does not gelatinise and in which intramolecular condensation would hardly take place, they found a drop in the iodine number of one-half which corresponds to the formation of a dimeric methyl ester having a formula such as the following:



$$\begin{array}{l} CH_3(CH_2)_3\underset{|}{CH} - \underset{|}{CH}.CH_2.CH_2.CH = CH(CH_2)_7.COO.OCH_3 \\ CH_3(CH_2)_3CH - CH.CH_2.CH_2.CH = CH(CH_2)_7.COO.OCH_3 \end{array}$$

In the case of China wood oil, assuming that the changes there are parallel to those occurring in the methyl ester, the drop in the iodine number at gelation corresponds to the formation of about 60% of a dimeric product. Consequently they believe that the dimeric trielaeostearate which forms during the heating is colloidally dissolved in the unchanged oil, and when it is formed in sufficient quantity it changes, through aggregation, into a solid.

They found that China wood oil could be gelatinised by the action of a 10 per cent. solution of hydrochloric acid in ether by careful regulation of the conditions, usually requiring about seven hours in the cold. The same solution dissolves China wood oil gels, so that the reaction is reversible. Hence they consider that the gel formation is due to the tendency of the heavy dipolymer to form aggregates. Hence they agree with

Wolff only as regards the last stage of the process.

They explain the fact that China wood oil gels while the methyl ester does not,although both undergo polymerisation, by assuming that the setting or gelatinising power of an oil is determined by the size or constitution of the alcohol with which the acid radicles are combined.

On oxidising the methyl ester of elaeostearic acid, Miller and Claxton (42) obtained two distinct fractions from the end product by extraction with petroleum ether. The insoluble fraction was a simple polymer of the soluble one as it had a molecular weight 3.86 times that of the latter even though it showed only slightly greater oxidation.

Further support for the views of Wolff is given by Auer (43) who states that the formation of boiled oil and the gelatinising of wood oil are of a colloidal nature and are part of the phenomenon of a coagulation. The determination of analytical constants appear to be influenced not only by chemical structure but also by colloidal reactions. Hence neither the molecular weight determinations,iodine numbers, viscosity,or refractive index are final proof for polymerisation during the boiling of fatty oils or during their film formation. A final proof, he claims, would be a demonstration of the presence of the 4-carbon-atom ring and a molecular weight determination in a true solution. He adds further that it seems improbable that a dimolecular polymerisation would occur in the presence of high molecular colloidal media. He considers that many so-called polymerisations are simply the coagulation of an isocolloid of a lyophilic nature.

Later (44) Auer showed that linseed oil dries in an atmosphere of carbon dioxide or in a partial vacuum due to a primary coagulation of the oil by gas similar to that of a lyophobic sol by an electrolyte. No drying was observed in a high vacuum. He says that when drying occurs in the open atmosphere the adsorption and coagulation are concurrent, chemical combination succeeding the adsorption.

Slansky (45) doubts the validity of Auer's "drying in vacuo" experiments and his consequent gas coagulation theory because he obtained no drying in vacuo over a period of 16 days. He mentions that the coagulation process leading to the solidification of drying oil films are subsequent to purely chemical reactions. Scheiber (46) and Scheifele (47) also oppose Auer's view.

Calderwood, Webb and Reihl (48) thickened oils without oxidation by heating and cooling in a filled, hermetically sealed, vessel connected through a sealing trap with supply and expansion vessels. This seems to support the coagulation theory.

Fonrobert and Pallauf (49) showed the possibilities of intramolecular and extramolecular polymerisation of the glycerides of elaeostearic acid by means of graphic formulae, and conclude that the reactivity of the partial valencies of elaeostearic acid leads to the formation of molecular complexes.

The same authors state (50) that the thickening and gelatinising of wood oil is a process involving re-esterification and polymerisation, the latter of the order of formaldehyde and phenol. It is, therefore, mainly of a chemical nature in which the viscosity increase is partly due to the glyceryl radicle as shown by the lowering of the viscosity when it is replaced by a monohydric alcohol.

By a determination of the molecular weight changes which take place during the boiling of linseed oil, using the freezing-point method in benzene (the same concentration being used throughout), Long and his co-workers (51,52,53) found that the apparent molecular weights increase tremendously depending upon various factors, e.g., the presence of driers. In one case the molecular weight rose from 722 to 3053. In general he noticed that the increase was much greater when air was allowed to enter than when it was excluded. They consider that intramolecular reactions with subsequent condensations are fundamentals of the changes taking place. They further found that the presence of sulphur, selenium, or tellurium suppressed the condensation tendency.

Bauer (54) observed that the molecular weights of polymerised linseed oil and perilla oil in camphor indicated a monomolecular compound and in benzene a dimer. He heated the α- and β-elaeostearic acids separately at 200°C. in an atmosphere of carbon dioxide. The molecular weight of the polymerised α-form was 4588 and of the β-form 985.6 when determined cryoscopically in benzene solution, and half those values in camphor. Long and Wentz (53), however, obtain comparable results using various solvents both in the case of linseed and China wood oils.

Long, Egge and Wetterau (55) found that in the case of linolenic monoglyceride, blowing at lower temperatures favors reactions which decrease the unsaturation with relatively small attendant increase in molecular weight. Heating at 293° C. favors condensation reactions.

Eibner and Munzert (56) establish that, in the usual process of setting of a drying oil, extramolecular polymerisation, which occurs during the thickening of oils by heat, is absent. The changes occuring during boiled-oil drying are more complex, not because of the formation of anhydrides or lactones but because of a rearrangement within the molecule of the fatty acids of the glyceride. In the films formed by the natural drying of the fatty oils the Rast camphor method showed no intramolecular autopolymerisation, but this is shown by boiled oils before drying. Hence they conclude that autoxidation, and possibly intramolecular polymerisation coupled with colloidal changes, comprise the stages in the normal process of drying. They consider that molecular weight determinations are dependent upon the degree of dispersion, the concentration of the solution, the character of the solvent, and the nature of the substance under examination. Furthermore they believe (57) that the dried films of linseed and China wood oils are solid solutions formed by a flocculation reaction. The amount and nature of the gels formed vary with the oil, the sols being glycerides of β-elaeostearic acid in the case of China wood oil and of α-and β-linolic acids in the case of linseed oil.

Marcusson (58) holds the same view as the above authors as he considers that unsaturated fatty acids unite at room temperature intramolecularly, whilst heat causes the reaction to become polymolecular. Isomerism is considered to occur before polymerisation, particularly in the case of tung oil (halogens and sulphur being catalysts for this isomerism). From determinations of the molecular weights of fractions isolated from linoxyn by the use of chloroform, acetone, and light petroleum, he finds that a linseed oil film consists of 55% of solid polymerised and oxidised gel, 40% of polymerised and oxidised sol, and 5% of unchanged oil.

In the case of tung oil, various investigators have found that solid masses are produced by heat polymerisation, freezing, and the action of light. According to Rasquin (59) the latter produces the true α- to β-change. As a guide to drying ability the iodine number is unreliable as Merz (60) has shown that α-elaeostearin is a better drying constituent of fatty oils than is linolenin. That fact should enhance the work of Böeseken and Ravenswaay (9) who showed that α -elaeostearic acid has three ethenoid linkages.

Morrell has criticised both the views of Salway (61) and of Wolff as regards the changes which take place during the thickening of drying oils by heat. The formation of a dimeride on the one hand and changes of aggregation of suspensoid material in a dispersion medium on the other are insufficient to explain the facts, and hence Morrell has stated that a compromise between the two theories should be considered. He bases this decision on two facts: firstly, the viscosity of the oil increases tremendously at the gelation point with hardly any change in the bromine value, thus emphasising the colloidal aspect; secondly, the special chemical characteristics of drying oils when heated. Poppy-seed oil and tung oil contain glycerides of linolic and elaeostearic acids respectively, differing only in the arrangement of the ethenoid linkages, yet the difference in their behaviour towards heat is very marked. Also in the thickening of linseed oil, which requires prolonged heating, there seems to be a shifting of the ethenoid linkages as he was unable to identify linolenic or linolic acids in the depolymerised oil. Using tung oil, where the heating is for a shorter period, the products obtained could easily be transformed into derivatives of the original elaeostearic acid.

Many of the phenomena which occur when China wood oil is thickened and coagulated by heat are comparable with the behaviour of a gelatin-water system. In tung oil the equilibrium of the thickened oil would seem to be at 50 per cent. of associated components, and any increase in the amount of these causes the system to set to a jelly. The gelation can be prevented by the presence of small quantities of apparently inert substances, rosin being the one most generally used. In other words, the rosin acts as a peptising agent. The addition of substances like glycerol or sulphur has a marked effect in preventing coagulation, one per cent. of sulphur and five per cent. of glycerin being sufficient to prevent solidification at 280°C.

In coagulated wood-oil jelly, which is formed, like all jellies, with an evolution of heat, the jelly is either a sponge or a honeycomb structure containing unchanged oil.

Summarising briefly, it is seen that the thickening of oils is connected with the presence of ethenoid linkages in special positions in the long carbon chain. Such unsaturated components have the power of forming aggregates, adsorbing the oil which is the dispersion medium, and remaining in a fluid condition depending on the temperature and the presence of small quantities of peptising agents.

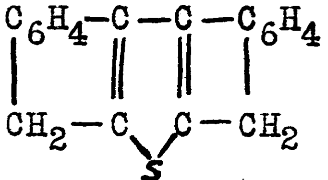
The Action of Sulphur on Unsaturated Organic Compounds

This subject is one which has received only a very slight amount of attention from organic chemists. What work there is shows that the reaction of sulphur with organic compounds does not always run smoothly as undesired by-products may be formed and so the reactions are often quite complicated. For example, tetraphenylthiophene (62) is formed by heating either phenylacetic acid or desoxybenzoin with sulphur at 220 to 260°C. Stilbene (63) is often formed as an intermediate compound, and it is able to form tetraphenylthiophene on being heated with sulphur at 250°C. or by passing in hydrogen sulphide at 260°C. In an analogous way cinnamic acid or styrene with sulphur yield two diphenylthiophenes,which Baumann and Fromm (64) consider structural isomers but which Steinkopf (65) believes are physical isomers.

By passing acetylene or ethylene through boiling sulphur Meyer (66) obtained a small quantity of thiophene, the main products being carbon, hydrogen sulphide, and carbon bisulphide. If, however, the sulphur is replaced (67) by finely-divided pyrites so that the reaction can go on slowly, a distillate is obtained containing about 40 per cent. thiophene. The formation of homologous thiophenes from homologous butadienes, for example the thiotolenes from isoprene (68),proceeds only at higher temperature in the manner indicated above by Meyer (66) and gives poorer yields.

In the case of acetylene the reaction is only one of addition, but in the case of butadiene and ethylene simultaneous oxidation is necessary.

Friedmann (69) made an investigation of the action of sulphur on indene, hydrindene, and cyclopentadiene. He heated one gram molecule of indene and one gram atom of sulphur at 180°C. and obtained two compounds, a diindenethiophene in which two molecules of indene were condensed with one atom of sulphur yielding



and also a substance having the formula $C_{36}H_{24}S$ which represents four indene molecules condensed with one atom of sulphur. By heating one gram molecule of indene with two gram atoms of sulphur at 180°C. a black compound $C_{36}H_{24}S_3$ was obtained, and at 210°C. a compound $C_{27}H_{20}S$. When one gram molecule of indene and one gram atom of sulphur were heated at 250°C., and then mixed with iron filings and heated to redness there collected on the upper part of the retort a compound $C_{44}H_{24}S$ or $C_{45}H_{24}S$, while the distillate contained a compound $C_{44}H_{32}S$ or $C_{45}H_{32}S$. The compounds obtained from indene and sulphur are asphalt-like in character.

The same author also found that hydrindene heated in a sealed tube with sulphur gave a compound $(C_9H_6)_2S$, and cyclopentadiene a compound $C_{10}H_{12}S$. These also seem to be condensation products of the original material with sulphur.

The Sulphurization of Oils.

Turning now to the setting of oils under the influence of sulphur and heat we find that Whitby and Chataway (1) have made the first systematic investigation, their work being carried out on linseed oil. They found three well-defined stages succeeding each other, namely, chemical combination of the sulphur with the oil, formation of an acetone-insoluble liquid, and gelation. With small proportions of sulphur (about 6%) the combination of the sulphur may be complete before the second stage begins. They observed that the rate at which the acetone-insoluble material forms and the maximum quantity obtainable at gelation increases with the proportion of sulphur present and with the temperature, and gelation takes place when a sufficient proportion of the sulphurised oil has become insoluble in acetone. Presumably during the heating the acetone-insoluble material gradually assumes colloidal dimensions, the colloidal material imbibes the acetone-soluble liquid and any portion of the acetone-insoluble portion which is still non-colloidal, and a gel then appears rather suddenly. The polymerising reaction, that is, the formation of acetone-insoluble material, was found to be irreversible. The authors also believe that the various species of triglyceride molecules present in linseed oil will undoubtedly behave differently with respect to the rate at which combination with sulphur and polymerisation of the sulphurised triglyceride takes place.

Molecular weight determinations of the acetone-soluble and acetone-insoluble fraction showed that the former was of the same order as that of the original oil, but that the latter indicated that polymerisation had occurred. This is similar to what is obtained in the blowing and heating of oils.

From a consideration of their results they decide that the mechanism of the setting of oils under the influence of air or heat or sulphur and heat are, in their main features, similar.

In all three cases an intermediate liquid product is formed which is soluble in ether or light petroleum, but is only partly soluble in acetone. The acetone-insoluble part was found to have a higher molecular weight than the acetone-soluble part thus indicating that polymerisation has occurred.

Furthermore, the taking up of oxygen or sulphur by the glycerides of drying oils greatly increases the polymerising tendency of such glycerides, so that, for example, polymerisation may occur in sulphurised linseed oil more quickly at 160°C than in raw oil at 280°C. Just as different sulphurised glycerides appear to require different temperatures in order to cause them to polymerise at an appreciable rate, so do the glycerides of raw oil possess different critical polymerisation temperatures as found by Morrell.

The authors further state that the views of Wolff and of Harries and Nagel that true chemical polymerisation in the case of the heating or blowing of oils does not occur, or at the most to a very small extent, and that the changes in molecular weight and iodine number are simply due to association is quite tenable owing to the disturbing way in which the molecular weights of the so-called polymerised oils vary with the concentration of the solution. It seems possible, they say, that the aggregates undergo disruption to a greater or less extent in different solvents.

Again, the authors point out that the gelation of the sulphurised oil is essentially a colloidal phenonenon as all the sulphur has reacted long before gelation occurs. Slansky, Schumann, and Marcusson have observed that the mere solidification of an oil, e.g., its transformation during the course of drying from a very viscous liquid to a solid, involves no change in the iodine number. The exact nature of this colloidal change is not yet known.

Recently Stamberger (70) has made several observations on the vulcanisation of oil. Using rapeseed oil and 20% sulphur he noticed that the reaction is strongly exothermic, the rise in temperature amounting to 5°C. Also a very small amount of hydrogen sulphide and sulphur-containing oil are given off.

He found that the vulcanisation of triolein proceeded the same as for rapeseed oil, and yielded a solid, sticky, very elastic mass. This could be divided into three parts, an acetone- soluble, a benzine-soluble, and a part insoluble in both solvents, but he observed that the acetone and benzine extraction could not be carried to a very sharp end-point and hence variations in the molecular weights of these fractions would occur. Their composition were identical and in close agreement with that of the isolated fatty acids. The molecular weight of the acetone-soluble part indicated a unimolecular size, that soluble in benzine corresponded to a dimeride, and the molecular weight of the fatty acids obtained by cold saponification of the benzine-insoluble part amounted to three times that of a sulphurised fatty acid. Hence the author considers that polymerisation has occured. The benzine-soluble fraction swells in benzene before it dissolves, whereas the insoluble portion swells about 700% without dissolving. The acetone-soluble and the benzine-soluble fractions become insoluble on long standing, by heating at 120-130°C., and through the action of sunlight or ultraviolet rays.

The sulphur content of the fatty acids obtained by saponification was about 2.5% lower than that in the glyceride. Hence he assumes that the difference was bound in the glyceryl residue.

From the above results the author states that the vulcanisation of oils proceeds in two sharply distinct steps: firstly, the formation of a sulphur compound of the oil in which the sulphur is chemically combined both in the fatty acids and in the glyceryl residue, and secondly, the polymerisation of this compound by further heating producing a corresponding change in its physical properties.

The above two-stage theory of vulcanisation is seen to bear out the work of Whitby and Chataway, and the third stage is lacking from his theory due to insufficient experimental data.

EXPERIMENTAL

Apparatus

For the purpose of carrying on this investigation a thermostat was made which could be regulated at any temperature, and was constant to ± 0.1° C. The heating elements were placed at the bottom of the oil bath and gave 14 ampéres when connected in parallel and 3.5 ampéres in series. It took one hour and a half to heat the bath up to 160°C.

Procedure

Samples of approximately 20 grams of the oil were weighted into stout Pyrex test-tubes, 25 cm. long, 3.4 cm. internal diameter, and having a 2 mm. wall. Definite percentages of sulphur were then put in and, when used, other materials such as accelerators, zinc oxide, etc., added in turn after it. The tubes were then placed in the oil bath, the surface of the oil in the tubes being about 2 inches below the surface of the oil in the bath. The oxygen of the air was excluded by the passage of a stream of carbon dioxide into the mouth of the tubes, the carbon dioxide being dried by bubbling it through concentrated sulphuric acid. The mixtures were stirred by means of heavy glass rods. thickened at the lower end, and connected to a small rotating wheel on a hot-air motor. At each rotation of the wheel the plungers touched the bottom of the tubes. The wheel was allowed to make about 130-135 revolutions per minute as faster stirring caused splashing. The temperature of the oil in the thermostat was kept constant to within ± 0.2°C.

At definite intervals samples of approximately one gram were removed from the tubes by means of small glass ladles. Each sample was placed in a weighed beaker and its weight determined. Twenty times its weight of acetone was then added from a burette and the mixture thoroughly stirred during the first half hour or so by means of a small glass rod, the beaker being covered with a watch-glass when not being stirred to prevent evaporation. One hour after the acetone was added the supernatant acetone was poured off and the beakers rinsed with 2 cc.

acetone. In the case of the samples taken very near gelation, especially when accelerators were used, the acetone was left in contact with the material an additional half hour with stirring as it seemed that a longer time would be needed for the extraction because of the dense character of the material. The stirrer was then washed off with ether into the viscous liquid or solid which remained in the beaker. This was allowed to stand overnight in an electric oven at 75°C., and then cooled and weighed.

The weight of this acetone-insoluble material was calculated as a percentage of the weight of the sample taken.

This percentage is merely an empirical value as will be seen from later remarks.

It may be stated that the acetone used was commercial acetone which was dried over calcium chloride and fractionated twice.

Accelerators

During the course of the work the following accelerators were employed:

1. Piperidinium pentamethylenedithiocarbamate
2. Zinc
3. Zinc phenylmethyldithiocarbamate
4. Zinc diethyldithiocarbamate
5. Zinc salt of the linseed oil fatty acids.

6. Isopropyl dixanthogen
7. Isopropyl monoxanthogen
8. Captax (mercaptobenzothiazol)
9. Grasselli 808
10. Zinc isopropyl xanthate
11. Diphenylguanidine
12. Aldehyde ammonia
13. P-nitrosodimethylaniline
14. Hexamethylenetetramine
15. Tetramethyl thiuram disulphide
16. Piperidine
17. Dibenzylamine

Of the above accelerators only a few were prepared by the writer as most of them are commercial samples. Piperidinium pentamethylenedithiocarbamate was prepared by dissolving 17 grams of piperidine in 150 c.c. of ether, the solution cooled, and a cold solution of carbon bisulphide in ether added to it with cooling. The product was filtered and dried. M.P. 162°C.

Zinc isopropyl xanthate was prepared by dissolving 10 grams of solium isopropyl xanthate in 100 c.c. of water and adding a dilute solution of zinc acetate. After filtering the material is washed well with water.

For the preparation of the zinc salt of the linseed oil fatty acids about 100 grams of the oil was hydrolysed with a slight excess of alcoholic potassium hydroxide. It was then acidified with dilute hydrochloric acid, and the fatty acid layer washed several times with hot water through which carbon dioxide was being bubbled. The fatty acids were now saponified again with a slight excess of alcoholic potassium hydroxide, and a dilute alcoholic solution of zinc chloride added to it. The material was filtered and washed well with alcohol and then with water.

Characteristics of the Linseed Oil

The characteristics of the second batch of linseed oil (from experiment 65 on) were the only ones determined as all of the first batch was used up in trying to get the most rapid time for gelation. In the case of the acid number equal quantities of benzene and alcohol were used to dissolve the oil as that is considered to reduce the degree of hydrolysis to a minimum.

Saponification number	190
Acid number	3.53

Abbreviations

To facilitate the writing-up of the tables it was thought best to abbreviate three words as they occurred so often. They are as follows:

P.P.	Piperidinium pentamethylenedithiocarbamate
Zinc P.	Zinc
G.	Gelled
*	Sulphur separated out on cooling (unless otherwise stated)

Note: Quantity of base used in the following experiments is equivalent only to the zinc salt of the accelerator (unless otherwise stated).

RESULTS

The first few experiments were really in the nature of trial runs in order to become acquainted with the procedure. However they proved of value in serving to indicate the following points:

1) Large stirrers with a flat bottom (three-quarters the diameter of the widest part) produce splashing unless slow stirring is employed. If small stirrers of a similar shape are used, more rapid stirring can be carried on, but the stirrers are not heavy enough to sink to the bottom of the oil with each revolution of the wheel when the oil becomes more viscous. Consequently long heavy plungers with a round thickened end were made, and the motor rotated at 130-135 revolutions per minute. This was found quite satisfactory.

2) In a few samples, after the initial quantity of acetone added had been poured off, the same quantity of fresh acetone was added, a control sample in each case being treated only once with acetone. The drop in weight was found to vary between 13 and 20% approximately when the quantity of acetone-insoluble material present after one extraction was over 45%. In the case of earlier samples, containing less acetone-insoluble material, the quantity dissolved by the second treatment was as high as 35%. This variation indicates that the smaller aggregates are more soluble in acetone than the larger ones. Also the fact that so much will dissolve out during the second treatment points

out how essential it is that the quantity of acetone added be exact, and shows why the percentage of acetone-insoluble material obtained is only an empirical value. Stamberger(70) has found that complete extraction with acetone or benzine could not be obtained within 48 hours.

Also, in a few cases, a sample was left exposed to the acetone for two hours instead of an hour. Instead of the expected decrease in weight on longer extraction there was an increase of 1.5 to 3% approximately. It was noticed that in the samples containing a large quantity of acetone-soluble material, 60 to 80%, a ring of acetone-soluble material always formed a short distance above the acetone. This must be due to a creeping of the acetone solution up the side of the beaker, and the evaporation of the acetone leaves this ring. Hence the increase in weight recorded above on longer extraction is due to an increase in this ring. At the start no special pains were taken to remove this ring during the rinsing, but from now on practically all of it was removed, the 2 cc. of acetone being run in slowly around the side of the beaker from a pipette.

3) In the case of the samples taken near the point of gelation the acetone-insoluble material was very viscous, and hence they were given a longer extraction, with stirring, in order to make sure that the maximum

quantity of acetone-soluble material was removed. Generally, in these cases, an extra half hour extraction was allowed. Very little creep was noticed in these samples, so no appreciable error could be introduced.

The following table is given to illustrate the second point mentioned, namely, that extracting once with acetone only gives an empirical relationship.

Table 1

Linseed oil + Sulphur at 160°C.

% Acetone-insoluble

		Expt.1	Expt.2	Expt.3	Expt.4	Expt.5	Expt.6	Expt.7
Sulphur		14%	14%	14%	12%	12%	12%	12%
Minutes								
45	A	31.1	30.5	30.7	19.2	19.3	18.3	19.5
	B		20.8	22.1			11.6	12.4
70	A	41.7						
95	A	48.5	45.9	46.4				
	B		36.6	37.0				
126	A	54.1						
	B	47.5						
	C	54.9						
130	A				43.1	44.0		43.3
	A							43.2
140	A	56.2	56.6	55.8				
	B	49.8	48.7					
	C	57.9						
156	A			60.0	46.9	47.3		
	B					40.6		
	C					48.1		
191	A				51.6	51.8	50.6	
	B					44.4	40.5	
	C				53.0	52.0		
211	A					53.6	52.3	51.1
	B						43.6	42.3
		G.in 159 m.	G.in 161 m.	G.in 163 m.		G.in 246 m.	G.in 250 m.	

A. Normal procedure. Acetone added in way described.
B. After decanting acetone, same quantity of fresh acetone added and stirred well.
C. Original acetone left for an additional hour with stirring.

Having obtained satisfactory stirring and an idea as to where the chances for error lay, it was now possible to begin a study of the effect of accelerators. Since nothing was known regarding the optimum temperature and the optimum proportion of materials to use in the case of oils, it was necessary to grope around in the dark for a time. The results obtained with a few common ultra-accelerators at 160°C. are as follows:

Table 11

Linseed oil + 12% Sulphur + Accelerator at 160°C.

% Acetone-insoluble.

	Expt.8	Expt.9	Expt.10	Expt.11	Expt.12
Zinc P.		2%			
Captax			2%		
Grasselli 808				2%	
P.P.					2%
Minutes					
90	37.6	40.5	37.4	31.0	42.0
150	48.0	49.5	46.5	43.1	51.0
210	54.8	54.8	52.5	49.1	58.2
240	58.5	56.7	55.6	51.8	
270				55.4	
	G.in 248 m.	G.in 269 m.	G.in 278 m.	G.in 334 m.	G.in 208 m.

As seen P.P. is the only one of the above ultra-accelerators to produce an acceleration at 160°C. The accelerators do not seem to change the quantity of acetone-insoluble material present at gelation. In the case of Zinc P. the retardation in the time of gelation seems to be due to a dispersive action which prevents the acetone-insoluble material from forming sufficiently large aggregates to enable gelation to occur. This dispersive effect may be due either to the accelerator itself or to its decomposition products. With Grasselli 808 the retardation appears to be caused chiefly by a slowing-up in the rate of sulphur combination.

In experiments #9 and #12 a white sublimate began to form around the top of the tube in about 6 to 8 minutes. It increased in quantity for a while, and then slowly passed away. It seems likely that the white sublimate is a carbonate of piperidine as it was later found that it did not form if the carbon dioxide was excluded from the tube.

The Zinc P. caused the material to assume a reddish-brown color.

Since, in the case of rubber, bases are known to enhance the action of accelerators, it was decided to try one here. The boiling-point of piperidine is 106°C., and so dibenzylamine which has a boiling point of 300°C. was used. The results obtained are compared with later results using piperidine.

Table 111

Linseed oil + 12% Sulphur + Accelerator + Base at 160°C.

% Acetone-insoluble

	Expt.13	Expt.14	Expt.15
Zinc P.	2%		
Zinc salt of linseed oil fatty acids			2%
P.P.		2%	
Piperidine			1 Equiv.
Dibenzylamine	1 Equiv.	1 Equiv.	
Minutes			
45			4.9
90	31.7	31.0	29.6
135			42.3
150	39.6	43.1	
180			53.2
210	44.9	49.1	
240	46.2	51.8	
270		55.4	
273	48.8		
305	50.1		
	G.in 455 m.	G.in 284 m.	G.in 185 m.

The results are surprising in that the same quantity of acetone-insoluble material is obtained in each case at the end of 90 minutes, and yet there is a tremendous variation in the time necessary for gelation to occur. By comparing with table 11 we see that the quantity of acetone-insoluble material present at the end of 90 minutes is less when the dibenzylamine is present. It appears likely that the combination of the sulphur is not the stage affected, and that the retardation is due to a dispersive influence exerted by the dibenzylamine which slows up the formation of aggregates necessary for gelation. This seems evident from the fact that the formation of acetone-insoluble material in the latter part of the sulphurization is very slow, and there is approximately the same amount present at gelation in each case. The material formed in experiment #13 is reddish-brown in color which is the same as was obtained in the absence of the base. The presence of the dibenzylamine does not prevent the formation of a white sublimate along the top of the tube in experiment #14.

Experiment #15 shows that piperidine does not exert a dispersive effect, and it will be shown later that piperidine enhances the action of the zinc salts of the accelerators.

TABLE 1V

Linseed oil + 12% Sulphur + P. P. + Zinc oxide at 160°C.

% Acetone-insoluble

	Expt.12	Expt.16	Expt.17	Expt.18	Expt.19	Expt.20	Expt.21
P. P.	2%	2%	2%			2%	2%
ZnO		5%	10%	5%	10%		5%
Minutes							
90	42.0	45.8	44.0	14.2		39.4	17.0
120						44.5	25.3
150	51.0	57.6		38.6	51.1	48.1	33.2
180		58.0	57.9			51.2	38.8
194			58.9				
210	58.2				59.7	55.7	42.4
240				51.4			
250							46.6
~~270~~							
	G.in 208 m.	G.in 199 m.	G.in 197 m.	G.in 293 m.	G.in 233 m.	G.in 234 m.	G.in 377 m.

* In experiment #20 the sulphur and accelerator were mixed together before adding them to the oil. In experiment #21 the sulphur, accelerator, and zinc oxide were mixed together before adding. In all other experiments, unless otherwise mentioned, the sulphur, accelerator, and zinc oxide were added in turn.

Large quantities of zinc oxide are thus seen to slightly activate P.P., but later it will be shown that 1 per cent. of zinc oxide is the optimum quantity ~~for~~ to use. Five per cent of zinc oxide alone produces a retardation, but this may be due to a decrease in the quantity of effective sulphur either through occlusion of the sulphur by the zinc oxide or by reacting with it. Ten per cent of zinc oxide shows a slight acceleration of its own, but this must be due to its action as a filler.

Experiments #20 and #21 show the effect of mixing the materials before adding it to the oil, a retardation being observed. The marked retardation in the case of experiment #21 must be due to the occlusion of some of the sulphur by the zinc oxide, a slight decrease in the quantity of available sulphur being sufficient to increase the time of gelation by the amount observed. Also the mixing would enable more sulphur to combine with the zinc oxide which would also cut down the concentration, but it seems that the first explanation is the main one.

No gas seems to be given off and no white sublimate is formed when 5 per cent of zinc oxide is present with the accelerator. The presence of the zinc oxide makes the material assume a brown color whereas the accelerator alone produces a cherry red color, a lighter cherry red color being obtained when only sulphur is used.

The effect of zinc oxide on captax was also determined, the sulphur, captax, and zinc oxide being mixed before adding them to the oil. At the time, the harmful effects of the mixing was not known, and experiments #20 and #21 in table lV were later run as a check on these.

TABLE V

Linseed oil + 12% Sulphur + Captax + Zinc oxide at 160°C.

% Acetone-insoluble

	Expt.10	*Expt.22	*Expt.23
Captax	2%	2%	4%
ZnO		5%	5%
Minutes			
90	37.4	43.3	18.0
120		48.0	25.1
150	46.5	50.6	
180		54.8	33.4
210	52.5	57.2	
240	55.6		38.6
273			
300			42.6
	G.in 278 m.	G.in 252 m.	Had not G. in 440 m.

*Material mixed before adding.

Zinc oxide is observed to cut down the retardation produced by captax, although its effect is only slight. No apparent reason can be given for the great retardation obtained with 4 per cent captax.

It might be mentioned that the oil assumes a light chocolate color due to the captax and zinc oxide, whereas captax alone does not affect the color which ordinarily is cherry red when sulphur is used alone.

From the above results it seemed that the accelerators which were used with rubber were not going to work well in the case of oils. Consequently it was thought desirable to try the effect of driers when sulphur was present as they are known to have a tremendous effect in accelerating the drying of an oil with oxygen.

TABLE Vl

Linseed oil - 12% Sulphur - Drier at 160°C..

	Expt.24	*Expt.25	Expt.26	Expt.27	Expt.28	Expt.29
Mn O				0.12%		1.63%
Mn O_2			0.16%		2%	
Mn resinate	2.17%	2.17%				
Minutes						
90	37.0	36.3	33.9	28.4	34.1	24.9
150	46.4	45.7	45.8	45.0	46.1	42.9
180	49.3					
210		50.4	54.5	53.9	51.8	50.6
240	61.2	61.6			56.2	56.4
273	74.4	69.8				
	G.in 292 m.	G.in 305 m.	G.in 245 m.	G.in 247 m.	G.in 255 m.	G.in 266 m.

* Sulphur and manganese resinate mixed before adding them to the oil.

In the first four experiments the quantity of drier used contained 0.1% of manganese as this had been found to give almost maximum results with oxygen. As seen, small amounts of manganese oxide and dioxide have no apparent effect on the time of gelation, whereas larger amounts exert a very slight retardation. Manganese resinate exerts a dispersive action as evidenced by the large amount of acetone-insoluble material present when gelation occurs, and this accounts for the longer time needed for gelation. Hence driers are of no value when sulpher is employed.

A couple of qualitative observations may be of interest. In the case of experiments #24 and #25 containing manganese resinate, it was very difficult to decant the acetone from the first two samples as the insoluble material had a tendency to run off too. The acetone-insoluble material of the last sample behaves like rubber, and the large quantity of insoluble material at gelation may be one of the reasons for this behaviour.

It has so far been shown that at 160°C., P. P. is the only accelerator that produces an acceleration in the time of gelation. In the case of rubber, accelerators have been found to work best at lower temperatures. Generally 125°C.to 141° C. is the optimum temperature, but in some instances, as in the dixanthogens and monoxanthogens, 110°-125° C. is best. Also some accelerators exert their effect over a wide range of temperatures whereas others are only effective over a very narrow range as in the dixanthogens and monoxanthogens. Consequently lower temperatures were now tried.

TABLE V11

Linseed oil + 20% Sulphur at various Temperatures

% Acetone-insoluble

	Expt.30	Expt.31	Expt.32	Expt.33
Temp.	160° C.	150°C.	140°C.	130° C.

Minutes				
63	51.9	25.6*		
90			3.40 ×	
115		58.9		
194				
255			56.2 □	*
273			58.1	
330				
375				42.4 □
420				48.0
465				56.1
490				57.2
	G.in 81 m.	G.in 120 m.	G.in 276 m.	G.in 505 m.

* Indicates sulphur has separated out on cooling.
× All sulphur. Separated out when sample cooled.
□ Material has assumed a cherry color.

The above results indicate that a rise of 10°C. reduces the time of gelation by almost a half. The amount of acetone-insoluble material at gelation does not appear to increase appreciably with the temperature. At lower temperatures there seems to be a pronounced induction in the rate at which the sulphur goes into combination, and no acetone-insoluble material appears to form until a definite quantity of sulphur has combined. That all the sulphur does not have to be combined before acetone-insoluble material forms is indicated by sample 1, experiment #31. The formation of acetone-insoluble material proceeds very slowly as the gelation point is approached, and this would indicate that aggregation or polymerisation was taking place slowly.

It must be pointed out that the taking out of samples before the sulphur is all dissolved changes the concentration of the mixture somewhat and hence the time of gelation. However these early samples are needed for comparative purposes, and may be made use of just as well as the time of gelation. This applies especially when accelerators are used as it is desirable to know just what stage of the process is affected. In any case the removal of these early samples can only affect the time of gelation very slighly when large proportions of sulphur are employed and a moderate amount of acetone-insoluble material has already formed indicating that a considerable quantity of sulphur has ~~already~~ combined.

At the same time as the above control experiments were carried out a similar set were run using an accelerator. The results are as follows:

TABLE V111

Linseed oil + 20% Sulphur + 5% Zinc phenylmethyldithiocarbamate + 3% Piperidine (1½ Equivalents)

% Acetone-insoluble

	Expt.34	Expt.35	Expt.36	Expt.37
Temp.	160° C.	150° C.	140° C.	130° C.
Minutes				
45	69.2			
63	69.9	60.8	49.6	45.3
76				
83		64.3		
90			60.9	50.0
100		73.3		
120				55.5
135			62.7	
150			64.7	58.3
165				59.6
195				60.2

G.in 88 m.	G.in 109 m.	G.in 170 m.	G.in 216 m.

The results obtained here are best realised by comparison with those of table Vll. The most obvious result is the marked decrease in the time of gelation at lower temperatures, whereas at higher temperatures the accelerator actually has a retarding effect, perhaps due to decomposition products. The effect of the accelerator appears to be twofold. It first increases the rate of sulphur combination at all the above temperatures, as is evidenced by the quantity of acetone-insoluble material formed at the end of 63 minutes and the fact that no sulphur separates from any of the samples on cooling. The second effect is a retardation in the time of gelation from this point to the end as the control samples gel more quickly than the accelerator samples from the time they contain as much acetone-insoluble material as the latter do at the end of 63 minutes. This is probably due to the dispersive action of either the accelerator itself, its decomposition products, or the zinc soaps formed by a reaction of the accelerator with the free acids present, and the fact that there is an increase in the quantity of acetone-insoluble material at gelation, especially at 150^{0} and 160^{0} C., would seem to prove this.

In most cases the decomposition products must exert a greater dispersive effect than the accelerator itself and more must decompose at higher temperatures as the differences in the quantity of acetone-insoluble material at gelation between the samples containing an accelerator and the controls are much greater. At those higher temperatures the increase in the rate of sulphur combination may be practically equal to the dispersive effect, and so the accelerator indicates little action if gauged by the time of setting, At lower temperatures this increase far overshadows the dispersive action.

Another striking point is the increase, with the temperatures, of the quantity of acetone-insoluble material present at gelation as compared to no appreciable variation in the control samples.

It may be mentioned that the sample containing an accelerator always looks much more viscous than the corresponding control sample. Also the material around the gelation point is generally somewhat elastic when hot, but its elasticity decreases greatly on cooling. Other polymerisable materials, such as meta-styrene, behave similarly. The elasticity of the material decreases on continued heating after gelation.

A white sublimate formed at the top of the tubes in the above four experiments. It formed more quickly and in greater amount at the higher temperatures, and in the next series of experiments it was shown that the amount is increased by using larger quantities of accelerator. When 1 per cent of zinc phenylmethyldthiocarbamate and one equivalent of piperidine are used there is only a small amount of white sublimate, but if only 1/2 equivalent of piperidine (or no piperidine) is present there is none at all indicating that piperidine is the cause of the formation.

The above results showed that with oils, as with rubber, accelerators do not produce good results at higher temperatures, and that above a certain temperature, which may vary with the accelerator, it is ineffective. At 160° C. a retarding effect was even observed. Consequently further work was now carried on at 140° C., and 20 per cent of sulphur was used in order to get rapid gelation. The optimum quantity of piperidine was the next point determined.

TABLE 1X

Linseed oil + 20% Sulphur + Zinc phenylmethyldithiocarbamate + Piperidine at 140° C.

% Acetone-insoluble

	Expt.38	Expt.39	Expt.40	Expt.41	Expt.36	Expt.42	Expt.43
Accelerator	1%	1%	1%	5%	5%	2%	2%
Piperidine	1/2 equiv.	1 equiv.	1-1/2 equiv.	1 equiv.	1-1/2 equiv.	1 equiv.	1-1/2 equiv.

Minutes							
45				50.5			
63			0.4	57.7	49.6	17.0	1.1
78				61.6			
90	0.9*	8.8*	0.4		60.9	38.0	1.1
98				65.0			
105				65.6			
120						58.2	
135	3.2*	33.0	7.0*		62.7		0.9
141						60.2	
144						60.9	
150					64.9		
165	14.6	47.1	16.5*				3.1*
197	25.1	57.7	26.4				9.4*
202		60.0					
255	55.9						
259	58.6						
300			55.5				28.0
	G.in 260 m.	G.in 204 m.	G.in 308 m.	G.in 108 m.	G.in 170 m.	G.in 145 m.	G.in 443 m.

* Sulphur present in acetone-insoluble material on drying. It did not separate out from the sample on cooling. Part of it may be zinc sulphide.

It is readily seen that, regardless of the quantity of accelerator used, one equivalent of piperidine gives the optimum results. Having less than one equivalent of base is not as detrimental as having more than one equivalent, but no regularity is observed in the effect of the excess base with increasing amounts of accelerator. Furthermore, two per cent. of accelerator plus one equivalent of piperidine is seen to be the most economical proportion to use for the results obtained.

The effect of increasing amounts of the accelerator plus the optimum quantity of piperidine is to increase the rate at which the sulphur combines with the oil. This in turn determines the rate at which acetone-insoluble material is going to form, and thus the time of gelation. The quantity of acetone-insoluble material at gelation also seems to increase slightly with increase in the quantity of accelerator. The effect of an excess or deficit of piperidine is to decrease the rate of combination of the sulphur, and also to decrease the quantity of acetone-insoluble material present at gelation, although this result is more pronounced with lower proportions of accelerator. Hence piperidine differs from dibenzylamine by retarding the sulphur combination and by exerting no dispersive action.

The following table is presented in order to compare the effect of zinc phenylmethyldithiocarbamate when used alone and when one equivalent of piperidine is added to it.

TABLE X

Linseed oil + 20% Sulphur + Zinc phenylmethyldithiocarbamate + Piperidine at 140° C.

% Acetone-insoluble

	Expt.32	Expt.44	Expt.45	Expt.39	Expt.42	Expt.41
Accelerator		1%	5%	1%	2%	5%
Piperidine				1 equiv.	1 equiv.	1 equiv.

Minutes						
45						50.5
63		2.94*	36.4		17.0	57.7
78						61.6
90	3.4*	10.3□	44.7	8.8□	38.0	
98						65.0
105						65.6
120					58.2	
135		34.1	53.2	33.0		
141					60.2	
144					60.9	
150			55.6			
165		46.7		47.1		
180			61.8			
197		57.7		57.7		
202				60.0		
255	56.2					
273	58.1					
	G.in 276 m.	G.in 210 m.	G.in 210 m.	G.in 204 m.	G.in 145 m.	G.in 108 m.

* Sulphur separated out on cooling.
□ Sulphur did not separate out. Present in acetone-insoluble material on drying; may be all zinc sulphide.

The most striking observation to be noted here is the marked activation which the piperidine exerts on the accelerator. This is not so obvious in the case of the one per cent. sample, but it seems likely that in this case there is a deficit of the accelerator, and if it is used up very quickly at the start the piperidine could not have much effect on it. The piperidine seems to aid the accelerator in still further cutting down the induction period for sulphur combination or else in increasing the rate of sulphur combination, either result being obtained by an activation of the accelerator itself.

By comparison with table 1X it is seen that a deficit or an excess of piperidine, with small amounts of accelerator, will retard the gelation as much, if not more, than the accelerator increases it.

Another interesting point in table X is the fact that the time of gelation in experiments #44 and #45 is the same, and yet there is a tremendous difference in the quantity of acetone-insoluble material at the end of 63 minutes. Hence the presence of excess accelerator seems to exert a dispersive action in retarding gelation, and this view is further borne out by the fact that the quantity of acetone-insoluble material present at gelation, when 5% of accelerator is used, is greater than with only 1%, this result being verified by experiments #41 and #42 when piperidine is used. It takes 120 minutes for the 2% sample to have as much acetone-insoluble material as the 5% sample has in 63 minutes, and yet there is only 38 minutes difference in the time of gelation. Consequently it seems that there is an optimum concentration of accelerator which would give the best results, that is, decrease the time for sulphur combination considerably and yet exert little dispersive action afterwards.

Since one equivalent of piperidine was found to activate the zinc salts of dithiocarbamic acid, it was decided to try its effect on P.P. and on mercaptobenzothiozol, commercially known as captax, and the results are compared with those later obtained using zinc isopropyl xanthate and other bases.

TABLE X1

Linseed oil + 20% Sulphur + Accelerator + Base at 140° C.

% Acetone-insoluble

	Expt.46	Expt.47	Expt.48	Expt.49	Expt.50	Expt.51
Mercaptobenzothiazol	2%	2%				
P.P.			2%	2%		
Zinc isopropyl xanthate					2%	2%
Piperidine		1 equiv.		1 equiv.		
Dibenzylamine						1 equiv.
Aniline					1 equiv.	
Minutes						
63	5.8*	9.6	7.5	0.9		
90	20.7*	25.3	31.5	10.8		
135	44.9	53.9	57.2	29.6		
145			60.6			
152		59.5	62.3			
154		61.9				
166	55.5					
175	57.7					
181	59.3					
202				62.1		
265						Some had formed
	G.in 183 m.	G.in 154 m.	G.in 154 m.	G.in 204 m.	Removed at 318 m.	Removed at 318 m.

* Sulphur separated out on cooling.

Piperidine acts as an activator for mercaptobenzothiazol, but not for P.P. In each case the presence of piperidine does not change the quantity of acetone-insoluble material present at gelation, but it does affect its rate of formation during the process. This may be due to an increased rate of sulphur combination in the case of mercaptobenzothiazol and a decreased rate in the second case. Using the same proportion of sulphur and the same temperature different accelerators seem to produce approximately the same quantity of acetone-insoluble material at gelation,

Piperidine has been found to activate in those cases where it can react with a zinc salt or can form an addition compound, as in the case of zinc isopropyl xanthate and captax respectively. With P.P. neither of these conditions are present.

Dibenzylamine and aniline both have a tremendous retarding effect. This is surprising in the case of dibenzylamine as it is quite a strong base. A large amount of sulphur was found at the bottom of each tube when they were removed indicating that these bases retard the sulphur combination greatly. The material in both tubes was much more viscous than the original oil showing that a change was going on, and it seems probable that both samples would have gelled if left long enough. By comparison with table 111 it appears likely that these bases cause more retardation at lower temperatures.

It seems a striking fact that no sulphur separated out from any of the samples which contained a base, and yet after five hours a large amount of sulphur was found at the bottom of the tubes containing aniline and dibenzylamine even in the presence of a powerful accelerator such as zinc isopropyl xanthate. Hence the obvious conclusion to draw is that the aniline and dibenzylamine decrease the solubility of the sulphur in the oil to a very marked extent at low temperatures, and thus the sulphur combination is retarded. This in turn retards the gelation. In the case of piperidine, one would assume from the results that it also affects the solubility of the sulphur except in those cases where it can work in conjunction with the accelerator.

It might be mentioned that no white sublimate was formed when captax was present alone or with piperidine.

In the experiments listed in tables 1V and V, 5% of zinc oxide was added as an activator because it is one of the usual quantities used in rubber, but as shown it did not give the same results as obtained with rubber. Since the experiments in table X seemed to indicate that an optimum ~~proportion of zinc oxide would produce activation~~ quantity of accelerator should be used, it was thought likely that an optimum proportion of zinc oxide would produce activation of an accelerator. This is now shown to be the case.

TABLE X11

Linseed oil + 20% Sulphur + P.P. + Zinc oxide at 140° C.

% Acetone-insoluble

	Expt.48	Expt.52	Expt.53	Expt.54	Expt.55	Expt.56
P.P.	2%	2%	2%	2%	2%	2%
Zn O		0.33%	1.0%	1.5%	2.0%	5.0%

Minutes						
45		2.3		7.7	2.0	
63	7.5	7.9	44.8	20.0	2.3	2.6
90	31.5	28.2	57.5	37.3	4.5	2.4
100			60.1			
115			63.8			
120		47.9	64.0			
130				51.7		
135	57.2					16.8
145	60.6	59.9		55.3		
150	61.9	63.2				
163				58.4		42.3
180					36.1	
195						58.5
199						63.1
221					55.1	
226					62.5	
	G.in 154 m.	G.in 151 m.	G.in 126 m.	G.in 166 m.	G.in 226 m.	G.in 199 m.

From the above it is seen that P.P. is quite a powerful accelerator for linseed oil as it cuts down the time of gelation at 140° C. by almost one half. About 1% of zinc oxide enhances the action of the accelerator somewhat, whereas larger quantities produce a retardation in the time of gelation.

The quantity of acetone-insoluble material present at the 63 minute period indicates that the activation produced by one per cent. of zinc oxide is due to a further reduction of the induction period or an increased rate of sulphur combination. A comparison of experiments #48 and #54 shows that the excess zinc oxide or the zinc soaps formed may exert a dispersive action, as experiment #54 has much more acetone-insoluble material at the end of 63 minutes and yet takes longer to gel. The quantity of acetone-insoluble material present at gelation varies somewhat with the proportion of zinc oxide used. One per cent. of zinc oxide causes more to be present than is formed in the presence of the accelerator alone, whereas larger amounts of zinc oxide show no difference. In the case of experiments #55 and #56, it is found that there is a sudden increase in the quantity of acetone-insoluble material at the gelation point, the increase being much greater than during a corresponding time just prior to the gelation. Other experiments might have given the same sudden increase if samples had been taken at the gelation point.

A white sublimate began to form in every one of the above cases in about 7 or 8 minutes.

When excess zinc oxide was used a hard cake was found at the bottom of each tube.

A lower temperature was next employed in order to see how P.P. acted at lower temperatures. At the same time the work would show whether the optimum proportion of zinc oxide changed with the temperature.

TABLE X111

** Linseed oil + 20% Sulphur + P.P. + Zinc oxide at 130°C.

% Acetone-insoluble

	Expt.57	Expt.58	Expt.59	Expt.60	Expt.61
P.P.	2%	2%	2%	2%	2%
Zn O	2.8%	1.0%	1.1%	1.2%	

Minutes					
63	4.4	15.8	5.5	1.7*	4.8*
90	10.4	26.1	18.3		3.9*
135	18.2	38.8			12.4
155			37.0	24.5	
185	26.1	49.6	48.3	42.6	
222			55.7	49.8	42.0
232			56.5		
238		58.3			
243		58.7			
256				55.7	
276					54.4
285					56.1
308	57.8				
	G.in 310 m.	G.in 244 m.	G.in 242 m.	G.in 265 m.	G.in 287 m.

** Fresh oil used.

These results show the great effect which small variations in the quantity of zinc oxide exert on the rate of gelation at low temperatures, and it is strange that about one per cent. is the optimum quantity, and that slight decreases or increases in that amount should affect the rate of gelation so decidedly. By comparison with Table X1 and X11, it will be noticed that a rise of 10° C. decreases the time of gelation by about half, and that the amount of acetone-insoluble material formed at gelation increases slightly with the temperature. This is exactly what has already been observed in Tables V11 and V111.

The white sublimate mentioned previously takes about twelve minutes to start forming instead of eight minutes at 140° C. indicating that the accelerator acts more slowly at lower temperatures, and this partly accounts for the increased time needed for gelation. At 160° C. it begins to form in about 5 minutes.

The material at this temperature remains tacky for over half an hour after gelation, whereas at 160° C. the material is non-tacky and brittle in about ten minutes. The material at the lower temperature seems to be more spongy and rubbery.

The speed with which the final gelation takes place, after the material seems to be on the point of gelation, varies with the materials added, their proportions, and the temperature. At 130° C. the sample containing 0.8 per cent. of zinc oxide goes through this final stage more quickly than the 1 per cent. sample.

TABLE X1V

Linseed oil + 20% Sulphur + Accelerator at 140° C.

	% Acetone-insoluble	
	Expt.52	Expt.62
P.P.	2%	
Zinc oxide	0.33%	
Zinc P.		1.57%
Piperidine		0.69%
Minutes		
45	2.3	7.8
63	7.9	21.3
90	28.2	43.3
120	47.9	
127		61.7
144	59.3	
149	62.6	
	G.in 151 m.	G.in 132 m.

The materials used in these two experiments are exactly equivalent as regards the quantity of zinc and piperidine present, but the results obtained are not the same. At the time the above experiments were run it was not known that one per cent. of zinc oxide was the optimum quantity in the presence of two per cent. of accelerator. With one per cent. of zinc oxide instead of 0.33% on the one hand and an equivalent quantity of material in the following experiment, identical results might be obtained.

Several experiments were now carried out to see if driers such as manganese oxide and manganese resinate would enhance the action of an accelerator at a low temperature. Also an attempt was made to accelerate the gelation after the sulphur was combined by using a polymerising agent such as zinc chloride aniline.

TABLE XV

Linseed oil + 20% Sulphur + P.P. + Drier at 130° C.

% Acetone-insoluble

	Expt.58	Expt.63	Expt.64	Expt.65	Expt.61
P.P.	2%	2%	2%	2%	2%
Drier	1%	0.87%	15.5%	1%	
	Zn O	Mn O	Mn resinate	Zn O	

Minutes					
63	15.8	6.1*	15.4		4.8
75				22.8	
77				1% zinc chloride aniline added (Only in Expt. 65)	
90	26.1	5.8*	27.3		3.9
120				38.6	
135	38.8	19.9*	44.4		12.4
155				45.0	
162					42.0
180		35.5	56.4		
185	49.6				
195				51.3	
203			60.2		
218			62.3		
225		46.3			
238	58.3			56.5	
240	~~58.7~~				
243	58.7			~~58.6~~	
249		~~55.9~~		58.6	~~54.2~~
275		55.9			54.2
	G.in 244 m.	G.in 284 m.	G.in 230 m.	G.in 255 m.	G.in 287 m.

N.B.- The amount of manganese oxide and resinate used above contained a quantity of manganese equivalent to the quantity of zinc in 1% of zinc oxide.

By comparing experiments #61 and #63 it is evident that manganese oxide does not activate the action of the accelerator. Manganese resinate produces the same activation as zinc oxide as indicated by the quantity of aceton-insoluble material formed at the end of 63 minutes, although it does cut down the time of gelation slightly more than the latter.

This experiment also yielded some very interesting qualitative observations which might be mentioned here. On sticking a stirring rod into the tube, and withdrawing, an ordinary sample gives a long, stringy material during the five minutes prior to gelation, yet in this experiment this long, stringy material was obtained for one hour and ten minutes after gelation. During a portion of the period the material was extremely elastic and could be stretched into a very fine thread about ten feet long without breaking; it was also practically non-tacky, seemed quite rubbery, and had considerable strength. Furthermore, it could be squeezed between the fingers without becoming tacky. Hence the manganese resinate must exert a softening effect, and this may be considered due entirely to the rosin it contains.

Since the accelerator seemed to aid the combination of the sulphur and had very little effect on the gelling of the product, it was thought likely that a polymerising agent might have some effect. Hence one per cent. of zinc chloride aniline was added after most of the sulphur was in combination, but a negligible result was obtained.

Using manganese oxide as an activator a large amount of the white sublimate mentioned previously formed at the top of the tube, whereas ~~the~~ with zinc oxide or manganese resinate only a small amount was observed.

TABLE XV1

Linseed oil + 20% Sulphur + Accelerator + Zinc oxide at 130° C.

% Acetone-insoluble

	Expt.66	Expt.61	Expt.67	Expt.68	Expt.69
Isopropyl dixanthogen	2%				2%
Isopropyl Monoxanthogen				2%	
Zinc diethyldithiocarbamate			2%		
P.P.		2%			
Zinc oxide				1%	1%
Minutes					
63		4.8*	4.8*		
90	7.3*	3.9*		7.2*	5.1*
135		12.4	12.3	18.1*	9.7*
180	7.0*			31.1	23.6*
220		41.5	37.5		
240				45.0	39.7
276	19.8*	54.4	50.8		
285		51.6		52.2	48.5
300			54.5		
304				54.6	
309			56.2		
317					53.9
330	36.4*				
395	50.1				
420	54.9				
	G.in 422 m.	G.in 287 m.	G.in 311 m.	G.in 308 m.	G.in 325 m.

At any temperature all accelerators do not show an equal accelerative action, and of course the same thing has been found by other investigators to apply in rubber. The presence of zinc oxide cuts down the time of gelation when isopropyl dixanthogen and monoxanthogen are used just as has already been shown with P.P. and captax, but the activation produced in the latter is not as great. The isopropyl monoxanthogen is slightly better than the dixanthogen, and the same thing has been found to hold in rubber. The quantity of acetone-insoluble material at gelation in the above experiments is approximately the same.

It was surprising that isopropyl dixanthogen and monoxanthogen did not produce greater acceleration than they did since they are very powerful accelerators. But in the case of rubber it has been found that they are effective over a very narrow range of temperatures, namely, between 110°- 125°C., as above that temperature they decompose. Consequently it was decided to try their effect at 116°C., using 1% of zinc oxide as an activator in one case and 1 equivalent of piperidine in the other. At the end of eight and a half hours the experiments were stopped as the materials were far from the gelation point, although they had turned cherry red and were more viscous than at the start. Hence we see that the temperature plays a very important role in the sulphurization of oils, more so than it does in rubber, and that below a certain temperature rapid gelation will not occur even in the presence of an accelerator. Considering the fact that solution of the sulphur takes place very slowly at low temperatures and the observation that the accelerator aids chiefly the combination of the sulphur, we can understand the above results.

TABLE XV11

Linseed oil + Sulphur + Accelerator, etc. at 125°C. and 140°C.

% Acetone-insoluble

	Temp. 125°C.		Temp.140°C.	
	Expt.70	Expt.81	Expt.72	Expt.73
Sulphur	20%	20%	14%	14%
Isopropyl dixanthogen	5.32%	2%	2%	
Zinc isopropyl-xanthate		4.12%		
Zinc diethyldi-thiocarbamate				2%
Zinc oxide	~~1%~~ 1%		1%	
Piperidine				1 equiv.
Minutes				
90			10.8	1.4
135	12.2*	15.6*	27.9	15.7
185	24.8*	28.4		
210			43.4	37.6
255	37.4	39.4		
270			51.4	47.8
330	51.1	50.4		
359	54.0	55.2		
	G.in 367 m.	G.in 368 m.	G.in 318 m.	G.in 358 m.

Since the results obtained at 116° C. using isopropyl dixanthogen were not very encouraging, a temperature of 125°C. was next employed as the accelerator decomposes above that temperature. By comparing with experiment #69, Table XV1, it is seen that the results are not as good ~~as~~ at 125° C. even though there is more accelerator present. In experiments #70 and #71, 3.32% of isopropyl dixanthigen plus 1% zinc oxide are equivalent to 4.12% zinc isopropyl zenthate.

Seeing that isopropyl dixanthogen gives better results at 130°C. than at 125°C. even though 130°C. is above the temperature at which it begins to decompose, an experiment was run at 140° C. Although zinc diethyldithiocarbamate, even without piperidine, was shown to work better than isopropyl dixanthogen plus zinc oxide at 130° C., the latter is more effective at 140° C. This is very surprising as isopropyl dixanthogen will not work at all in the case of rubber at that temperature.

Since zinc oxide was found to activate P.P., it was thought that zinc in a more soluble form would give even better results. Hence the zinc salt of the fatty acids in linseed oil was prepared.

TABLE XV111

Linseed oil + 20% Sulphur + P.P. + Zinc salt of the fatty acids in linseed oil at 140° C.

% Acetone-insoluble

	Expt.74	Expt.75	Expt.76	Expt.48	Expt.77	Expt.78	Expt.79
P.P.	2%	2%	2%	2%	2%	2%	2%
Zinc salt	1%	2%	5%		1%zinc salt, 1%zinc oxide	2%zinc salt, 2equiv. piperidine	2%zinc salt, 1equiv. piperidine
Minutes							
45							38.8
63	20.0	40.0	17.6	7.5	7.6	44.8	49.5
90	43.0	52.9	38.0	31.5	17.3	53.6	54.8
110							57.9
117		55.9	47.4				
120	55.9				29.3	55.2	
129	57.6	58.8					
135				57.2			
145				60.6			
151				62.1			
170			58.9				
177					55.2		
	G.in 138 m.	G.in 136 m.	G.in 179 m.	G.in 154 m.	G.in 182 m.	G.in 136 m.	G.in 127 m.

This table brings out several very interesting points. Two per cent. of the zinc salt of the linseed oil fatty acids produces the greatest initial activation of the accelerator as evidenced by the quantity of acetone-insoluble material at the end of 63 minutes, and yet 1 per cent. gives the same time of gelation as 2 per cent. Also 1 per cent . and 5 per cent. produce the same result at the end of 63 minutes, but the 5 per cent. sample takes much longer to gel. These results indicate that the zinc salt has a twofold effect. It first enhances the action of ~~ator~~ the accelerator, and then serves to disperse the acetone-insoluble material and thus retard gelation. If the zinc salt is used up during the activation of the accelerator we can see why 1 per cent. of the zinc salt has little dispersive power as it may be almost all used up at the start.

As shown previously, and also as indicated by experiment #77, having too much zinc present is worse than having none at all. Its main effect seems to be a retardation of the sulphur combination.

The presence of piperidine seems to have little effect, 1 equivalent producing a slight activation, whereas 2 equivalents have no effect whatever. This is especially remarkable as a considerable excess has been used, and it was shown in Table 111 that an excess of piperidine exerted a considerable retardation.

Since the zinc salt of the linseed oil fatty acids in the presence of piperidine is shown in Table XIX to be just as good an accelerator as P.P. itself, the results here show that a combination of accelerators is better than each accelerator alone. The combination of accelerators, in all cases shown, seems to aid chiefly the combination of the sulphur.

Gelation came very slowly in experiments #75, #78, and #79 after the material was exceedingly viscous, and an examination of the amounts of acetone-insoluble material present during those experiments as compared with some of the others bears this out.

In the last set of experiemtns it was shown that the zinc salt of the linseed oil fatty acids did activate P.P., but the activation is not as much as that produced by zinc oxide unless one equivalent of piperidine (calculated on the amount of zinc salt) is also present. The next point to determine was whether the zinc salt would act as an accelerator alone.

TABLE X1X

Linseed oil + 20% Sulphur + Zinc salt of the linseed oil fatty acids + Piperidine at 140°C.

% Acetone-insoluble

	Expt.80	Expt.81	Expt.82	Expt.83
Zinc salt	2%	3.5%	5.15%	7.7%
Piperidine	1 equiv.	1 equiv.	1 equiv.	1 equiv.
Minutes				
45	1.1*	3.3*	1.0*	3.6*
63	5.5	14.8		
75			5.6	10.0
90	20.0	38.5	22.1	28.1
138	50.0	57.6		
145			55.3	53.2
178				58.6
	G.in 160 m.	G.in 146 m.	G.in 160 m.	G.in 188 m.

These results indicate that the zinc salt of the linseed oil fatty acids is a very good accelerator when 1 equivalent of piperidine is present. Whether it would work just as well without the piperidine has not been determined. In the above, 2 per cent. of the zinc salt contains a quantity of zinc equivalent to the acid number of the oil, 7.7 per cent, the same quantity as 1 per cent. zinc oxide, 5.15 percent. represents a quantity of zinc equal to the zinc present in 1 per cent. zinc oxide less the quantity of zinc necessary to react with 2 per cent. P.P. if all the accelerator is used up in that way, 3.5 per cent. of the zinc salt represents an intermediate amount. As seen, this intermediate quantity of zinc gives the best result. Since the zinc salt is entirely soluble in the oil and the zinc oxide not nearly so soluble, it appears that some of the zinc oxide is not used up during the reaction or else it has an additional function such as reacting with the P.P.

By comparison with Table XV111 a striking observation is the fact that the formation of acetone-insoluble material proceeds at the same rate in experiments #48 and #81, and that the initial formation of acetone-insoluble material here is much slower than in, say, experiments #75 and #79. Hence the induction period for sulphur combination does not seem to be entirely removed in the former experiments, or else the rate of sulphur combination is much smaller. The latter explanation seems the more likely one.

The experiments recorded in the following three tables endeavoured to show if the accelerators aided the sulphur combination more at lower temperatures.

TABLE XX

Linseed oil + 20 % Sulphur + 2% P.P. + 2% Zinc salt of the linseed oil fatty acids + 1 equivalent Piperidine

% Acetone-insoluble

	Expt.79	Expt.84	Expt.85	Expt.86
Temp.	140°C.	150°C.	140°C.for 1/2 hr.Then raised to 150°C. in 12 min.	140°C.for 1/2 hr.Then raised to 150°C. in 12 min.Then raised to 160°C. in 12 min.
Minutes				
30			11.68	14.9
45	38.8	14.9	35.7	40.8
63	49.5	27.7	51.8	57.8
73				63.0
81		46.5		
84			60.6	
90	54.8			
102		57.9		
110	57.9			
	G.in 127 m.	G.in 109 m.	G.in 93 m.	G.in 84 m.

These results indicate that the accelerator produces more rapid combination of the sulphur at a lower temperature, but that the further changes which lead towards gelation take place more rapidly at a higher temperature. However, by comparing with Tables XXl and XXll, we see that this is not universally true of accelerators as in those cases the higher temperature is conducive to more rapid combination of the sulphur as gauged by the quantity of acetone-insoluble material formed at the end of 30 minutes.

TABLE XX1

Linseed oil + 20% Sulphur + 2% Isopropyl dixanthogen + 2% Zinc isopropyl xanthate + 1 equivalent Piperidine

% Acetone-insoluble

	Expt.87	Expt.88	Expt.89	Expt.90
Temp.	140°C.	140°C.for 1/2 hr.Then raised to 150°C.in 12 min.	150°C.for 1/2 hr.Then raised to 160°C.in 12 min.	160°C.
Minutes				
30		2.8*	19.6	53.4
40				67.4
42				69.8
45		5.5	51.1	
57			68.3	
63	14.9	28.7		
90	35.2	55.4		
115	48.1			
	G.in 140 m.	G.in 97 m.	G.in 60 m.	G.in 43 m.

TABLE XX11

Linseed oil + 20% Sulphur + 2% Zinc salt of the linseed oil fatty acids + 1 equivalent Piperidine

% Acetone-insoluble

	Expt.91	Expt.80
Temp.	140°C.	150°C.for 1/2 hr. Then raised to 160°C. in 12 min.
Minutes		
30		8.3
45	1.1*	40.3
63	5.5	
90	20.0	
138	50	
	G.in 140 m.	G.in 65 m.

As regards the experiments recorded in the last three tables, it may be stated that gelation came very quickly only in the case of the four experiments listed in Table XX1, that is, the material gelled in a very short time after it became extremely viscous.

A study was now made of the effect of varying the proportion of sulphur on the sulphurisation of linseed oil.

TABLE XX111

Linseed oil + Sulphur + 2% Isopropyl dixanthogen + 2% Zinc isopropyl xanthate + 1 equivalent Piperidine at 160°C.

% Acetone-insoluble

	Expt.92	Expt.93	Expt.94	Expt.95	Expt.96	Expt.90	Expt.97
Sulphur	12%	14%	14%	16%	18%	20%	20%
Minutes							
30		8.0	13.3	2.2	38.6	53.4	51.3
40						67.4	
42						69.8	
45	2.6	21.2	21.6	14.7	53.3		65.4
49							66.6
59					58.3		
64					60.1		
90	26.1	45.3	46.9	46.7			
102				59.8			
123		55.5	55.7				
135	40.2						
180	49.0						
204	53.3						
	G.in 209 m.	G.in 130 m.	G.in 126 m.	G.in 102 m.	G.in 65 m.	G.in 43 m.	G.in 51 m.

No isopropyl dixanthogen in experiment#97

The great decrease in the time of gelation with increasing proportions of sulphur is very noticeable. The quantity of acetone-insoluble material formed at gelation increses slightly up to 18% sulphur, and then rises more sharply. The 16% sulphur experiment does not seem to fit in the series as regards the quantity of acetone-insoluble material formed after 30 minutes, but the 14% sulphur sample was checked and gave quite concorant results.

A very striking point is the tremendous increase in acetone-insoluble material formed at the end of 30 minutes in the case of the 18% and 20% sulphur experiments.

Experiment #97 again shows that a single accelerator is not as effective as a combination of two accelerators. As before, the added decrease in the time of gelation due to the second accelerator is not very great.

In order to speed up the work several samples were weighed up the day before making the run. However, one of the results did not fall in line with previous results, and on checking these experiments it was found that allowing the material to stand over-night had an effect in some cases.

TABLE XXlV

Linseed oil + Sulphur + Accelerator + Piperidine

% Acetone-insoluble

	At 140° C.		At 160° C.			
	Expt.98	Expt.80	Expt.99	Expt.95	Expt.100	Expt.96
Sulphur	20%	20%	16%	16%	18%	18%
Zinc salt of linseed oil fatty acids	2%	2%				
Piperidine	1 equiv.	1 equiv.				
Isopropyl dixanthogen			2%	2%	2%	2%
Zinc isopropyl xanthate			2%	2%	2%	2%
Piperidine			1 equiv.	1 equiv.	1 equiv.	1 equiv.
Minutes						
30			0.9	2.2	27.4	38.6
45	1.2*	1.1*	7.4	14.7	42.3	53.3
59						58.3
63	8.9*	5.5	18.1		55.1	
64						60.1
90		20.0	36.8	46.7		
102				59.8		
110						
128			55.9			
138		50.0				
140	57.1					
	G.in 155 m.	G.in 160 m.	G.in 131 m.	G.in 102 m.	G.in 74 m.	G.in 65 m.

N.B. Experiments #98, #99, and #100---material weighed out, added to the oil, and left over-night.

The results indicated by this table are very interesting as we see that in one case weighing out the material the previous day has no effect on the time of gelation, whereas in the other two it has. Now, in table XVlll, it was shown that piperidine did not seem to activate the zinc salt of the linseed oil fatty acids appreciably, whereas it was previously found that piperidine did enhance the action of the zinc dithiocarbamates, and hence it must activate zinc isopropyl xanthate. The activation seems to be due to a reaction between the two, and such a reaction taking place over-night would, in all probability, affect the quantity of accelerator available when the heating was carried on.

Another explanation appears likely. It was found that when the samples were left corked over-night that the inside of the tubes were sticky. A thin film of piperidine there would cause that stickiness, and it seems possible that some of the piperidine evaporated from the oil and condensed along the side of the tube. Since it has already been shown that unless exactly one equivalent of piperidine was present the optimum results would not be obtained, except in the case of the zinc salts of the linseed oil fatty acids, it is evident why a variation would occur in one sample on standing and not in the other.

Several experiments were now carried out at 180°C. to see if gelation would occur with low percentages of sulphur.

TABLE XXV

Linseed oil + Sulphur + Isopropyl dixanthogen + Zinc isopropyl xanthate + Piperidine at 180°C.

% Acetone-insoluble

	Expt.101	Expt.102	Expt.103	Expt.104
Sulphur	12%	12%	8%	6%
Isopropyl dixanthogen		2%		
Zinc isopropyl xanthate		2%		
Piperidine		1 equiv.		
Minutes				
30	28.0	0.4	None	None
46	41.2	0.3		
74	54.0			
90		21.3	None	None
145		51.8		
180			17.5	12.1
360			40.3	28.7
480			46.8	34.6
520			50.5	
	G.in 82 m.	G.in 153 m.	G.in 537 m.	Had not G.in 638 m.

Raising the temperature 20° C. cuts down the time of gelation of a 12 per cent. sample from 248 minutes at 160 °C. to 82 minutes at 180° C. The accelerator must decompose very rapidly at that high temperature, and its decomposition products greatly retard the gelation. They appear to do that by retarding the combination of the sulphur as the quantity of acetone-insoluble material formed in experiment #101 and #102 at the end of 30 minutes and 90 minutes respectively are approximately the same, and the material in each experiment gels in about the same time from this point.

Experiments #103 and #104 are interesting in that they show that gelation will occur with small quantities of sulphur. The 6% sulphur experiment was not carried to completion, but it is very probable that it would gel if heated long enough. A very rapid stream of carbon dioxide was passed into the mouth of the tubes to make sure that no appreciable quantities of air would enter. When the tube containing the 6% sulphur sample was removed from the bath and cooled, the material was found to be extremely viscous.

At gelation the 8 per cent. sulphur sample had hardly any body ~~to it~~ in contrast to what is obtained at lower temperatures, especially in the presence of accelerators. Heating the material containing 8 per cent. sulphur after gelation causes it to become denser and to have some bulk, but the material is very tacky. The acetone-insoluble material of all the samples taken in experiments #103 and #104 were soluble in ether.

As observed previously, over 50 per cent. of acetone-insoluble material must be formed before gelation occurs. It must be remembered that this is simply an empirical value.

A number of control experiments for those listed in table XXIII were now to be run, but unfortunately the oil and sulphur gave out. When the new materials arrived it was decided to spend some time in studying one set of experiments in detail, in order to see whether the accelerator only affected the sulphur combination or also the last part of the process.

The first point to be determined was at what time in the process at 140° C. the sulphur was all combined, both in the presence of an accelerator and in the control. Chataway(1) had found that at 160° C. all the sulphur was combined in 45 minutes. Since P.P. is a powerful accelerator and leaves no residue it was considered a satisfactory one to use. Table XXVl gives the results obtained the first time.

TABLE XXVl

**Linseed oil + 20% Sulphur + P.P. at 140° C.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.105	Expt.106	Expt.105	Expt.106
P.P.	2%			
Minutes				
45	7.0*		2.2*	
55	14.9*		1.4*	
63	22.0*		.8*	
90	44.2		None	
123	56.7		28.5	
131		10.4*		1.43*
143		16.6*		0.6*
155		25.1*		0.2*
175		36.8*		Negligible*
210		52.0		12.1
	G.in 128 m.	G.in 225 m.		

* Sulphur separated out on allowing sample to stand for some time.
** Fresh oil.

The ether-insoluble material was obtained by adding twenty times its weight of ether to the sample, stirring well several times, decanting at the end of an hour, and then rinsing twice with 2 c.c. of ether. It was found to be very jelly-like.

No ether-insoluble material is obtained until almost 50% of acetone-insoluble material has formed. Hence at the start all the ether-insoluble material present represents dissolved sulphur. Therefore in the tube containing the accelerator dissolved sulphur is present in the oil for about 80 minutes whereas in the control it is present for 175 minutes, and it may be pointed out that the difference almost corresponds to the difference in the time of gelation.

The fact that there is dissolved sulphur in the oil when over 30% of acetone-insoluble material is present indicates that acetone-insoluble material can begin to form as soon as a definite percentage of sulphur is combined.

The variation in the time of gelation obtained here and those given previously may be due either to a change in the concentration of the mixtures due to the removal of so many samples before the sulphur is all dissolved and combined, or else to the fact that the fresh oil has a slightly different composition from the previous one. By comparison with table XXVIII it is seen that the second assumption is the main one as the control given in that table takes less time to gel than before. Hence the results shown in this table and in

Error in Numbering Pages

later experiments cannot be compared with previous results.

In experiment #105 it was shown that when 20% of sulphur is used in the presence of an accelerator, 2.2% of dissolved sulphur is present at the end of 45 minutes. Consequently it was thought that by starting with 16% of sulphur none would be uncombined in 45 minutes,

TABLE XXV11

Linseed oil + 16% Sulphur + P.P. at 140° C.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.107	Expt.108	Expt.107	Expt.108
P.P.	2%			
Minutes				
35	2.5*		1.3*	
45	2.8*		1.7*	
55	3.3*		0.8*	
63	7.9*		Negligible*	
80	16.3		None	
105	30.0		"	
127		1.8*		
138		2.9*		
152		6.6 *		
165	55.2		14.6	
180		16.9		None
240		46.9		"
267		55.7		20.6
	G.in 177 m.	G.in 275 m.		

The result obtained was unexpected as dissolved sulphur was present in both samples almost as long as before. Hence this indicated that the sulphur combination was a time reaction, the rate varying with the temperature and with the amount of sulphur.

The quantity of acetone-insoluble material present when all the sulphur disappears is much less than when 20 per cent. of sulphur was used, and is not changed by the presence of an accelerator.

Having found the point at which only a negligible quantity of sulphur is dissolved in the oil, 2% of an accelerator was added at that point. A control experiment was run at the same time.

TABLE XXV111

Linseed oil + 20 % Sulphur at 140° C. 2% of P. P. added 166 minutes after the start.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.109	Expt.110	Expt.109	Expt.110
Minutes				
143		11.1*		0.06*
165		25.0*		0.05*
166	2% of P.P. added		2% of P.P. added	
180	55.0	33.9	1.9	None
195	63.0		33.7	
205	67.4		42.5	
212			45.5	
225		55.2		17.5
	G.in 212 m.	G.in 234 m.		

Fourteen minutes after the accelerator was added the appearance of that sample had changed tremendously compared to the control. It had more bulk than the control sample 9 minutes before gelation. Contrary to what happens when the accelerator is present right from the start there was a great increase in the quantity of acetone-insoluble material at gelation in this case. As seen, there is a hastening of the gelation, but the decrease is not very great due chiefly to the slow rate at which the last part of the process takes place giving a very indeterminate end-point. This may be due to a dispersive effect exerted by excess accelerator. Very likely if only, say, 1% of accelerator had been added the slow rate of gelation after the material became extremely viscous would not have been so prominent.

After about 50 per cent. of acetone-insoluble material has formed the formation of ether-insoluble material takes place at a very rapid rate, and so it is the main factor in the production of a gel.

Before drawing the conclusion that the accelerator aids the last part of the process as well as the combination of the sulphur, it was decided to try a few more experiments on similar lines. In one experiment 4% P.P. was added at the start; in the other 2% was added at the start and two per cent. more when the sulphur was all combined as found in experiment #105.

TABLE XXlX

Linseed oil + 20% Sulphur + P.P. at 140° C.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.111	Expt.112	Expt.111	Expt.112
P. P.	4%	2% at the start 2% after 76 minutes		
Minutes				
45	5.7		0.17	
55	13.5		Negligible	
76		2% of accelerator added		2% of accelerator added
~~90~~				
~~115~~ 90	48.0	53.5	0.6	2.5
~~120~~ 115	59.4	61.3	28.4	27.3
~~126~~ 120			32.3	
~~131~~ 126			39.4	
~~141~~ 131	74.7		49.0	
~~158~~ 141				41.9
153				52.2
	G.in 128 m.	G.in 148 m.		

The conclusions arrived at here are obtained by comparison with tables XXVl and XXV111. Although 4 per cent. of the accelerator causes a disappearance of the dissolved sulphur about 25 minutes before that in the 2 per cent. sample, yet the two samples have the same time of gelation. Furthermore there is a marked increase in the quantity of acetone-insoluble and ether-insoluble material at gelation in the case of the 4 per cent. sample, and hence it seems that the additional 2 per cent. of accelerator or its decomposition products must exert a dispersive effect and thus retard the gelation. This seems to be borne out by experiment #112 as the addition of 2 per cent. of accelerator after there is no dissolved sulphur present causes a retardation of 20 minutes in the time of gelation, with consequent increase in the quantity of acetone-insoluble and ether-insoluble material. Also in experiment #109 it seems that the addition of 2 per cent. of accelerator after there is no dissolved sulphur left is an excess as a marked slowing up of the gelation occurs after the initial accelerating effect. Hence a smaller quantity of accelerator in that experiment would likely produce better results.

It may be pointed out that the initial acceleration produced in experiments #109 and #112 on adding 2 per cent. of accelerator after the dissolved sulphur has combined is approximately the same, ~~and~~ In both cases the end-point is very indeterminate and gelation occurs extremely slowly, the result of this being a large increase in the amount of acetone-insoluble and ether-insoluble material at gelation.

Experiments #105 and #111 which have 2 per cent. and 4 per cent. of accelerator respectively also have the same quantity of acetone-insoluble material after 55 minutes, and yet in the 4 per cent. sample there is no dissolved sulphur present at that time. Hence within certain narrow limits the rate of formation of acetone-insoluble material does not seem to depend on the quantity of sulphur combined.

After gelation the amount of acetone-insoluble and ether-insoluble material continue to increase.

More white sublimate is formed around the top of the tube in the case of the 4 per cent. sample than in the 2 per cent. sample.

For the purpose of getting more information as regards the sulphur combination experiments #107 and #108 were repeated, and a determination made of the quantity of undissolved and dissolved sulphur present in the tubes at various periods of time. The procedure followed was as follows: Two tubes were placed in the bath. At the end of, say, 25 minutes a sample was taken from one tube for the determination of acetone-insoluble and ether-insoluble material. A minute later the tube was removed, a layer of liquid sulphur being found at the bottom. The bottom of the tube was cooled causing this sulphur to solidify in one mass. On allowing the material to stand for a day or two the uncombined sulphur, which had been dissolved, crystallized out, and on extracting the material with ether the undissolved and uncombined sulphur remained. The undissolved mass was in one solid lump and could be removed from the crystalline material. After washing well with ether the weight of each was determined, and a correction added to the amount of dissolved sulphur owing to the sample removed. A similar procedure was followed at other periods of time, the results being recorded in the next table.

TABLE XXX

Linseed oil + 16% Sulphur + P. P. at 140° C.

P. P. 2%

Minutes	% Acetone-insoluble		% Ether-insoluble		% Sulphur undissolved		% Sulphur dissolved but/ uncombined		% of original Sulphur combined	
	Expt. 113	Expt. 114	Expt. 113	Expt. 114	Expt. 113	Expt. 114	Expt. 113	Expt. 114	Expt. 113	Expt. 114
25	2.76		1.25							
27					7.00		2.25		42.2	
35	2.11		0.92							
45	1.55		0.07							
46					5.42		2.46		50.8	
60	0.06		None							
61					4.10		1.44		65.4	
82	2.92		None							
83					3.78		0.86		71.0	
138		5.6		0.09						
139						1.15		3.24		72.6
163		15.8		None						
165						0.36		1.13		90.8

N.B. The sulphur remaining at the various periods of time is calculated as a percentage of the original oil.

These results are very important as they show that the combination of the sulphur is a time reaction regardless of whether an accelerator is present. At the start, in the presence of an accelerator, only 42% of the sulphur combines in 27 minutes, 51% in 46 minutes, 65% in 61 minutes, and 71% in 83 minutes. ~~Consequently, after a rapid start, there seems to be a lag in the rate of sulphur combination.~~ In 83 minutes the sample containing the accelerator has as much sulphur combined as the control in an hour longer. But it was shown previously that the difference in the time of gelation was over 1 hour and a half. Hence this indicates that the accelerator

.does accelerate the last part of the process, and table XXXll appears to bear this out.

It may be noticed that of the uncombined sulphur there is always more of the sulphur undissolved than dissolved when the accelerator is present, whereas the reverse holds true in the absence of the accelerator. It appears probable that solution of the sulphur is the slow process, and that the accelerator only aids the combination of the sulphur. In doing so, however, it continually destroys the equilibrium between dissolved and undissolved sulphur, and hence the accelerator increases the whole process. Further work along this line would be very helpful in drawing a complete picture.

Seeing that there was still 1-1/2 per cent. uncombined sulphur present at the end of 165 minutes when only 16 per cent. was used at the start, it seems that more might have been present at that time if 20 per cent. had been used instead. Hence the acceleration obtained in experiment #109 when 2 per cent. of accelerator was added after the sulphur was thought to be all combined may have been due to a more rapid combination of this uncombined sulphur. Since Chataway had found that all the sulphur was combined in 45 minutes at 160° C., it was decided to repeat experiment #109 using only 14 per cent. of sulphur and heating at 160° C. until all the sulphur was combined. Then the material was to be cooled to 140° C. and 2 per cent of accelerator added. By running a control at the same time it would thus be possible to, see if the accelerator aided the last part of the process leading to gelation after all the sulphur was combined.

In order to see how soon the sulphur would be combined two tubes containing linseed oil and 14 per cent. of sulphur were placed in the bath at 160° C. After 45 minutes a sample was removed from one tube, the tube removed the next minute, cooled, and the proprotion of undissolved and dissolved sulphur determined as before. At the end of 80 minutes a similar procedure was followed with the material in the second tube.
The results obtained were as follows:

TABLE XXXI

Linseed oil + 14% Sulphur at 160° C.

	% Acetone-insoluble	% Ether-insoluble	% Sulphur undissolved	% Sulphur dissolved but not combined	% of original Sulphur combined
	Expt.115	Expt.115	Expt.115	Expt.115	Expt.115
Minutes					
45	6.4	None			
46			5.01	0.008	64.2
80	30.0	None			
81			0.23	None	98.4

By comparison with experiment #114 we see that the rate of sulphur combination is much greater at 160° C. than at 140° C., but even at the higher temperature it takes considerable time. Contrary to what was found at 140° C., very little dissolved sulphur is present even though there is a considerable quantity of undissolved sulphur. This leads to the conclusion that at 160° C. combination of the sulphur takes place as soon as it dissolves, and that solution of the sulphur is a slow process even at that temperature. At 140° C. combination of the sulphur takes place much more slowly, and so there is always a considerable amount of dissolved sulphur present. The accelerator seems to aid only the combination of the sulphur, but by producing a faster removal of the sulphur more is caused to go into solution.

Having found that practically all the sulphur combines at 160° C. in about 80 minutes when 14% of sulphur is used, it was now possible to determine if the accelerator aids the last portion of the process by adding, say, 2 per cent. after the sulphur was all combined, a control being run at the same time. Since accelerators work best at lower temperatures, 140° C. was considered a satisfactory temperature at which to add the accelerator. Consequently experiment #115 was repeated and the oil heated with 14 per cent, of sulphur for 109 minutes. The tubes were removed from the bath, and the latter cooled down to 140° C. in one hour. They were then replaced, and five minutes allowed for the materials to heat up again. After an additional 11 minutes heating 2 per cent. of P.P. was added to one tube with stirring. The results obtained were as follows:

TABLE XXX11

Linseed oil + 14% Sulphur. Heated at 160°C. for 109 minutes.
Tubes removed and then heated further at 140°C.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.116	Expt.117	Expt.116	Expt.117
Minutes				
108	35.7		None	
109	Tubes removed and bath cooled to 140°C.			
120		2% P.P. added		2% P.P. added
135	45.2	53.5	None	30.7
168	49.3	54.8	None	35.7
	G.in 228 m.	G.in 193 m.		

When the tubes were removed from the bath a very small amount of sulphur was noticed at the bottom, but the quantity was negligible as it was much smaller than that found in experiment #115 after 81 minutes. An extremely small amount of sulphur was noticed at gelation at the bottom of the tube which contained no accelerator, whereas in the other tube none could be seen.

The accelerator does seem to have an immediate effect on the material when added as seen by the increased formation of acetone-insoluble and ether-insoluble material and by the greater bulk of the samples as compared with the corresponding control samples, but it causes the material to have a very slow and indeterminate end-point. It does make the material less tacky and more elastic at gelation. The time of setting was reduced one-third from the time the accelerator was added. This result was also obtained in experiment #109 using 20 per cent. of sulphur.

** EXPERIMENT 118

Although the results of experiments #109 and #117 seemed to prove that the accelerator did produce a noticeable effect on the sulphurised oil after the sulphur was all combined, there was always the possibility that a small amount of free sulphur might ~~of~~ have been present, and this of course would affect the result. Consequently a large batch of linseed oil was heated with 20% of sulphur at 140 C. for 186 minutes, and the sulphurised oil extracted with dried ether in order to remove any uncombined sulphur (only a very small quantity was found). The ether was then removed in vacuo, and portions of the residue heated as follows:

**Fresh oil used.

TABLE XXX111

Temp.	140°C.				130°C.	
	% Acetone-insoluble		% Ether-insoluble			
	Expt.119	Expt.120	Expt.119	Expt.120	Expt.121	Expt.122
P.P.		1%		1%		1%
Minutes						
0	46.0		0.0			
10	50.9	49.9	2.6	17.0		
15	53.3	51.0	8.1	38.5		
20		54.4		43.1		
31	57.1		27.7			
35				46.6		
41			30.2			
66			41.7			
76		65.4		57.1		
90	63.1		49.3			
	G.in 35 m.	G.in 23 m.			G.in 50 m.	G.in 26 m.

The above results are very important as they furnish positive proof that the accelerator does hasten the last part of the process after about 46 per cent of acetone-insoluble material has formed, even though there is no free sulphur present. Although a decrease of one-third is obtained at 140°C., the actual shortening in the time of setting during this part of the process is very small. The main effect of the accelerator at this stage is in producing a tremendous increase in the rate of formation of the ether-insoluble material, that is, the large aggregates. Experiment #120 was as far advanced one minute after gelation as experiment #119 was 15 minutes after setting as regards bulk, tackiness, etc.

A rise of 10°C. does not change the effect of the accelerator during the last stage, and hence in the presence of an accelerator changes of temperature mainly affect the rate of combination of the sulphur and the rate of formation of the acetone-insoluble material.

The solubility in benzene and in ether of the products obtained in table XXX111 was as follows:

TABLE XXX1V

	Solubility in Benzene		Solubility in Ether	
Minutes	Expt.119	Expt.120	Expt.119	Expt.120
23		Almost completely soluble		Considerable quantity insoluble
35	Completely soluble	Considerable quantity insoluble	↑	
			Considerable quantity insoluble	
50	Almost completely soluble			
95	Considerable quantity insoluble			

The material insoluble in benzene was in a swollen condition, whereas that insoluble in ether was not. In the case of experiment #121, the material was still completely soluble in benzene after 125 minutes, i.e., 75 minutes after gelation. This is a further example of the effect of temperature on the last stage of the process.

It has just been stated that the material in experiment #120 was as far advanced one minute after gelation as the control sample was 15 minutes after gelation as regards bulk, tackiness, etc., and an inspection of table XXX11 indicates that at those two points the quantity of ether-insoluble material was of the same magnitude. Also the solubility in benzene at those two periods was shown in table XXX1V to be about the same.

EXPERIMENT 123

The next point to determine was whether the accelerator would have any effect on the acetone-soluble portion of the sulphurised oil. Hence another large batch of linseed oil was heated with 20% of sulphur at 140°C. for 186 minutes, and this time the sulphurised oil was well extracted with successive quantities of acetone. The acetone-insoluble material remaining was a spongy solid. It may be mentioned that the acetone-insoluble material was now partly insoluble in ether, whereas before the extraction it was completely soluble. The acetone was removed in vacuo from the acetone-insoluble material, and the latter heated as follows:

TABLE XXXV

Temperature 140°C.

% Acetone-insoluble

	Expt.124	Expt.125	Expt.126	Expt.127
Sulphur			10%	10%
P.P.		1%		1%
Minutes				
60			49.4	58.3
275	43.9	37.5		
360	50.7	43.2		
	G.in 378 m.	G.in 480 m.	G.in 96 m.	G.in 69 m.

The acetone-soluble material must have contained a considerable amount of sulphur in combination to enable gelation to occur. A surprising feature is the retardation produced by the accelerator. Again it is observed that over 50 per cent. of acetone-insoluble material must be formed before gelation takes place.

Experiments #126 and #127 indicate that the sulphurised oil can take up sulphur at a rapid rate, and the accelerator is again observed to function. The final end-point came quickly in these experiments, whereas it was very slow indeed without the additional 10 per cent. of sulphur.

EXPERIMENT 128

In order to get a large quantity of sulphur in combination quickly so as to avoid, as much as possible, the changes taking place in the sulphurised oil during the heating, it was decided to heat linseed oil with 30 per cent. of sulphur at 160°C. Gelation occurs in this case in 34 minutes, and preliminary work indicated that 20 per cent. of sulphur was combined at the end of 29 minutes whereas only 11.5 per cent. was combined after 22 minutes.

A large batch of linseed oil was heated with 30 per cemt. of sulphur at 160°C. for 25 minutes, and cooled quickly. This material was then extracted with dried ether, and 15.2 per cent. of sulphur was found to be in combination. The ether was removed in vacuo, and the residue heated as follows:

TABLE XXXV1

Temperature 140°C.

	% Acetone-insoluble		% Ether-insoluble	
	Expt.129	Expt.130	Expt.129	Expt.130
P.P.		1%		1%
Minutes				
15	18.6	23.2		
60	31.2	35.8		
120	42.3	43.2		
150			None	None
	G.in 247 m.	G.in 246 m.		

Althoughthe material in experiment #130 appeared much denser than the control at the end of 15 minutes, nevertheless there is very little difference in the quantity of acetone-insoluble material present at that time in the two experiments. Also we notice that the rate of formation ~~forming~~ of acetone-insoluble material in the control is slightly greater than in the experiment containing the P.P., and so it seems that the accelerator slightly retards the formation of the acetone-insoluble material. However its retardation during this stage is offset by the greater rate of formation of the ether-insoluble material during the following stage, and so in this case the time of setting is the same.

EXPERIMENT 131

Part of the ether-soluble material prepared in experiment #128 was heated in two tubes (30 grams in each) for 70 minutes at 140°C. so that about 33 per cent. of acetone-insoluble material would be present. It was then cooled and extracted well with acetone using successive quantities of 150,150,75, 75, and 50 c.c. in each tube, that is, 13 times its weight. The acetone-insoluble material remaining was jelly-like in character and extremely viscous. It would barely flow.

Tube I — Heated to 140°C.

Material did not liquefy on heating, and in four minutes it had taken the appearance of the ordinary gelled material 10 minutes after setting. It was tacky.

Tube II - 1% of P.P. added - Heated to 140°C.

Material became non-tacky immediately (within two minutes) and did not change in appearance on continued heating for 30 minutes. It could be rubbed to soft separate particles throughout that period. The material in tube I reached that non-tacky and powdery stage in 50 minutes.

EXPERIMENT 132

The last experiment was repeated, but this time less acetone was employed for the extraction (100 c.c. and 75 c.c. used successively, which represents about five times its weight of acetone). The acetone-insoluble material this time was quite fluid.

Tube I - Heated to 140°C.

Gelation occurred in about 7 minutes.

Tube II - 1% P.P. added - Heated to 140°C.

Material gelled in about three minutes.

The material obtained in the last experiment at gelation is more tacky than that in experiment #131, especially so in the presence of the accelerator.

EXPERIMENT 133

Experiment #131 was again repeated, but this time only 50 c.c. of acetone was used for the extraction of 16 grams of material, that is, 2.5 times its weight of acetone was employed.

There was only enough material left for one tube.

Tube I - 1% P.P. added - Heated at 140°C.

Gelation occurred in 78 minutes, an indeterminate end-point being obtained. The material was extremely tacky at gelation as a sort of fluid gel was formed.

From the last few experiments it is readily seen that the acetone-soluble material plays a great part in retarding the setting of the sulphurised oil. Simply extracting with 2.5 times its weight of acetone produces a reduction in the time of setting of almost two-thirds from that point, whereas using five times its weight in two successive quantities causes almost instantaneous gelation at 140°C.

It was thought desirable to carry out a few more experiments on similar lines.

EXPERIMENT 134

Experiment #128 was repeated, linseed oil being heated with 30 per cent. of sulphur at 160°C. for 25 minutes. On extracting with dried ether it was found that there was 16.2 per cent. of combined sulphur present. The ether was removed in vacuo, and the residue heated as follows:

TABLE XXXV11

	% Acetone-insoluble			
	Expt.135	Expt.136	Expt.137	Expt.138
Temp.	140°C.	140°C.	160°C.	160°C.
P.P.		1%		1%
Minutes				
15	25.0	26.5		
60	37.6			
	G.in 179 m.	G.in 202 m.	G.in 71 m.	G.in 80 m.

The results shown verify those in table XXXV1 by proving that the accelerator does not enhance the formation of the acetone-insoluble material even though ~~there~~ there appears to be a marked increase in the bulk. The retardation produced during this stage is greater than the accelerating effect it exhibits during the succeeding stage in which the ether-insoluble material is formed, and so the accelerator, on the whole, shows a slight retardation.

A rise in temperature produces a marked decrease in the time of setting of the sulphurised oil.

EXPERIMENT 139

Part of the ether-soluble material prepared in the previous experiment was heated for 1 hour at 140°C. in order to increase the quantity of acetone-insoluble material. It was then cooled and extracted with 2.5 times its weight of acetone. The insoluble material was placed in two tubes and heated.

Error in Numbering Pages

TABLE XXXV111

Temperature 140°C.

% Ether-insoluble material

	Expt.140	Expt.141
P.P.		1%
Minutes 15	None	None
	G.in 35 m.	G.in 31 m.

The acetone-insoluble material remaining above after extraction had acetone dissolved in it. When only 1.3 times its weight of acetone had been added a homogeneous solution was obtained. Hence this seems to indicate that sulphurised linseed oil has a two-phase structure, and that when acetone is added it increases the proportion of one of the phases until the critical amount is reached. Further addition of acetone then causes a separation of the two phases, the completeness of the separation depending on the proportion of acetone added.

EXPERIMENT 142

Experiment #128 was again repeated, but this time linseed oil was heated with 30 per cent. of sulphur for 29 minutes, and cooled quickly. The material was extracted with dried ether, the amount of combined sulphur thus found to be 18.2%. The ether was distilled in vacuo, and the sulphurised oil heated as follows:

TABLE XXX1X

	Temperature 140°C.						Temp. 160°C.	
	% Acetone-insoluble			% Ether-insoluble				
	Expt. 143	Expt. 144	Expt. 145	Expt. 143	Expt. 144	Expt. 145	Expt. 146	Expt. 147
P.P.		1%			1%			
Minutes								
15	36.3	37.9		None	None			
60	47.4	51.7	1% P.P. added	None	1.1	1% P.P. added		
75			53.8			0.4		
	G.in 125 m.	G.in 122 m.	G.in 124 m.				G.in 50 m.	G.in 50 m.

Even though there is a higher proportion of combined sulphur present this time the result obtained is no different from that obtained in the last three tables. This indicates that the accelerator does not aid the gelation of the sulphurised oil. But it was seen in table XXX111 that the accelerator does aid the formation of ether-insoluble material which represents the last stage before gelation. Hence it seems that in experiment #118 the prolonged heating at 140 C. must have enabled some change to take place in the oil thus making it more subject to the presence of an accelerator.

However, in experiment #145 no increase in the formation of ether-insoluble material is observed, and in that case the accelerator was added after the heating had been carried on at 140°C.for some time. Consequently the heating at 160°C. may have produced some retarding effect. No definite conclusion can be drawn as regards the effect of the accelerator on the later stages of the sulphurisation process until some further experiments are carried out.

It might be mentioned here that the material in experiment #145 appeared markedly denser after the accelerat~~ion~~or was added even though there was no increase in the quantity of ether-insoluble material or any shortening in the time of gelation.

Determination of Molecular Weights

Molecular weight determinations were made of the material during experiment #119, this material having been obtained by heating linseed oil with 20 per cent of sulphur at 140°C. for 186 minutes and extracting with ether.

TABLE XL

Time of heating (Min. after extraction)	Conc. %	Depression (in Degrees)	Molecular Wt.
0	2.66	.101	1314
	3.48	.131	1330
	6.10	.239	1277
15	2.02	.072	1400
	2.84	.099	1432
28	1.97	.063	1565
	4.28	.137	1600

The molecular weight of the sulphurised oil is observed to increase slowly on continued heating, and does does not vary with the concentration ~~contration~~. The results indicate that polymerisation of the sulphurised oil has occurred.

TABLE XL1

Expt. No.	Time of heating (Minutes)	Conc.	Depression	Mol. Wt.
129	15	1.94	.087	1114
129	15	3.99	.175	1140
*130	15	2.01	.082	1226
*131 (tube 11)	2.5	1.84	.077	1194
132 (" 1)	7.5	0.645	.0145	2227
132 (" 1)	7.5	1.86	.040	2330
*132 (" 11)	3.5	1.82	.113	806

*Indicates that P.P. was present during the heating.

Again we find that the molecular weights do not vary appreciably with the concentration. This seems to be further evidence of polymerisation. The fact that #4 and #7 have such low molecular weights compared to #6 must be due to the presence of the accelerator in the benzene solution.

The acetone-insoluble material obtained in experiment #123, which was a spongy solid, was dried in vacuo. Only a part of it dissolved in benzene, the remainder being in a swollen state. The molecular weight of the soluble part was 1555, the concentration of the solution being 0.96%.

In addition to this instance it has been observed a number of times that extraction with acetone makes the residue partly insoluble in other solvents.

At this stage it was thought desirable to examine the effect of sulphur on China wood oil with and without an accelerator, and some very interesting results were obtained.

TABLE XL11

China wood oil + Sulphur at 140°C.

Expt.No.	% Sulphur	Minutes
148	12	102
149	14	82
150	16	88

China wood oil is thus seen to produce more rapid gelation than linseed oil even using much smaller proportions of sulphur. Also the effect of varying the proportion of sulphur does not produce such marked differences as in linseed oil.

TABLE XL111

China wood oil + Sulphur + Accelerator at 140°C.

Expt.No.	% sulphur	% P.P.	Minutes
151	10	2	123
152	12	1	108
153	13	1	93
154	14	1	13.5
155	14	0.5	39
156	16	1	14.5
157	16	2	14

By comparison with the previous table we see that the accelerator shows a marked effect only when 14 per cent. of sulphur is present, but that then there is an enormous effect quite comparable with the acceleration produced in rubber by the same accelerator when zinc oxide is not present. A definite amount of accelerator is needed to produce the best results, but this amount is much lower than when linseed oil is used. Whether a large excess would not give as good results as the optimum amount was not determined.

In the case of experiment #154 the material was very fluid at the end of 12 minutes, and looked no different than the original oil in this respect, and yet one minute later it had considerable body and appeared on the point of setting. A little sulphur was found at the bottom of the tube at gelation, but not nearly as much as when 16 per cent. of sulphur was used.

The material in experiment #151 containing 10 per cent. of sulphur had a much darker cherry red color in 7 minutes than the 16 per cent. control had in 65 minutes, and yet took much longer to gel. It was quite viscous after 20 minutes and near gelation, but the last stage took place very slowly and gave an indeterminate end-point. The material was also very tacky when it gelled. Using 12 per cent. of sulphur with an accelerator the final gelation point comes comparatively quickly, but the material is still very tacky.

When 14 or 16 per cent. of sulphur is employed in the presence of an accelerator the material not only gels so much faster due to the additional 2 per cent. of sulphur, but is also non-tacky at gelation. Furthermore, it is practically non-elastic as it cannot be stretched without breaking. Hence the tackiness is either a function of the unsaturation, the time of heating, or the size of the aggregates. Using only 0.5 per cent. of the accelerator takes the material three times as long to gel, and it is quite tacky at gelation. With 14 per cent. of sulphur and 1 per cent. of accelerator the material is transparent at gelation, whereas if heated with 12 per cent. of sulphur plus accelerator it is much darker in color and not apparently transparent.

When 12 per cent. of sulphur is used with and without an accelerator at the end of 45 minutes the mixture containing the accelerator is quite viscous whereas the control is very fluid. At the end of 75 minutes it was only slightly more viscous than the control. Nevertheless the control sample gelled sooner, and the final gelling came very quickly in it and much more slowly in the mixture containing the accelerator.

The work on China wood oil was halted for about five weeks, and then it was found that the oil had become partially oxidised and that slightly over 12 per cent. of sulphur, instead of 14 per cent., was sufficient to give optimum results. The effect of adding various materials and varying the temperature was now studied.

TABLE XLIV

China wood oil + 10% Sulphur at 140°C.

Expt.No.	P.P. %	Zn O %	Piperidine	Miscellaneous %	Time (Min.)
158					100
159	1				98
160	1	1			90
161	1	5			44
162		5			105
163			2%		127
164				1% Zinc P.	81
165			1 Equiv.	1% " "	102
166			2 "	1% " "	121
167				2% oleic acid	97
168				2% " "	96

The results tabulated above are difficult to understand. Using 10 per cent. of sulphur, that is, an amount of sulphur less than that required to give the optimum results, it is found that the addition of an accelerator or its activator has very little effect. The only real activation that is obtained is by the use of a large quantity of zinc oxide with P.P. Even the presence of one equivalent of piperidine does not enhance the action of zinc P. Hence the results obtained using china wood oil with a deficit of sulphur are not, on the whole, in agreement with those of linseed oil under the same conditions.

TABLE XLV

China wood oil + 15% Sulphur at 140°C.

Expt.No.	P.P. %	ZnO %	Piperidine	Miscellaneous %	Time (Min.)
169					68
170	1				13.5
171	1	1			13.5
172	1	5			18
173		5			70
174			2%		10.5
175				1% Zinc Pip.	17.5
176			1 Equiv.	1% " "	11.5
177			2 "	1% " "	9.5
178			1 "	3% " "	9.5
179			2 "	3% " "	9.5
180				2% oleic acid	65
181	1			2% " "	12.5
182				2% linoleic acid	64

With an excess of sulphur, that is, 15 per cent., the results fall more in line with those obtained using linseed oil. P.P. and zinc P. are observed to produce a marked acceleration. However the effect of the accelerators are much more striking with china wood oil, the results obtained approaching the acceleration produced in rubber. The presence of an excess of piperidine with zinc P. does not exert a retardation, but the reason is apparent as piperidine alone acts as a powerful accelerator when an excess of sulphur is present. Why it should not do so with a deficit of sulphur is unexplainable. The presence of oleic acid does not affect the result obtained without it. The oil is not so subject to variations in the per cent. of zinc oxide added when an excess of sulphur is used, whereas zinc oxide alone shows no effect in either case.

TABLE XLV1

China wood oil + Sulphur at various Temperatures

Expt.No.	Temp.	Sulphur %	P.P. %	ZnO %	Miscellaneous %	Time (Min.)
183	140	12	1			18
184	140	12	1	1		18
185	140	17			10% oleic acid	66
186	140	17			10% linoleic"	59
187	130	15				144
169	140	15				68
189	160	15				20
188	130	15	1			18
170	140	15	1			13.5
190	160	15	1			18
158	140	10				100
191	160	10				37.5
159	140	10	1			98
192	160	10	1			54

In the control samples there is a noticeable reduction in the time of setting with rise in temperature both in case of an excess and a deficit of sulphur. The effect is quite comparable to that found with linseed oil. When an accelerator is present with an excess of sulphur very little variation with the temperature in the time of gelation is observed, but with a deficit of sulphur the results again are similar to those obtained with linseed oil.

Large quantities of oleic and linoleic acids do not affect the rate of gelation if sufficient excess sulphur is present to take care of their unsaturation.

In the case of experiment No.192, the sulphur combined very quickly but the formation of acetone-insoluble material was observed to be slow.

TABLE XLVII

China wood oil at 140°C.

% acetone-insoluble

	Expt. 193	Expt. 194	Expt.195	Expt.196
Sulphur	15%	15%	10%	10%
P.P.	1%		1%	
Minutes				
08	19.5*			
10	34.6			
11	48.4			
22			29.2	
35		9.2*		
45			36.8	5.3
50		25.4*		
60		41.4*		
65		50.5*		
75			45.3	28.5
88			49.4	~~46.2~~
96				46.2
	G.in 11 m.	G.in 66 m.	G.in 88 m.	G.in 98 m.

* Sulphur separated out on cooling.

These experiments indicate that the quantity of acetone-insoluble material required before gelation occurs is of the same order as that for linseed oil, although the actual amount is somewhat lower.

Having observed marked variations in the results obtained with china wood oil using an excess and a deficit of sulphur, a set of similar experiments were run with linseed oil to see if the same conditions held there.

TABLE XLVIII

Linseed oil + 20% Sulphur at 140°C.

Expt. No.	P.P. %	Zn O %	Piperidine	Miscellaneous %	Time (Min.)
197					215
198	1				134
199	2				129
200	2	1			136
201	2	5			130
202		5			201
203			2%		134
204				2% Zinc P.	144
205			1 Equiv.	2% " "	119
206			2 "	2% " "	133
207				2% oleic acid	224

Although a deficit of sulphur has been used above the results obtained are practically identical with those in table XLV using an excess of sulphur with china wood oil, although, as mentioned previously, the magnitude of the effect of the accelerators and their activators is not nearly as great with linseed oil. The only difference noted is the fact that two equivalents of piperidine is not as efficient as one equivalent in the case of linseed oil , whereas no variation was observed with china wood oil.

TABLE XL1X

Linseed oil + 25% Sulphur at 140°C.

Expt.No.	P.P. %	ZnO %	Piperidine	Miscellaneous %	Time (Min.)
208					166
209	1				95
210	2				89
211	2	1			76
212	2	5			74
213		5			164
214			2%		89
215				2% Zinc P.	80
216			1 Equiv.	2% " "	68
217			2 "	2% " "	75

The results obtained in the above table using an excess of sulphur are practically identical with those in table XLVIII where a deficit of sulphur was employed, whereas this similarity was not obtained with china wood oil.

TABLE L

Linseed oil + Sulphur at 140°C.

Expt. No.	Sulphur %	P.P. %	Time (Min.)
218	22		184
219	23		174
220	30		157
221	35		150
222	30	2	76
223	35	2	73

Even when an excess of sulphur is present the time of setting is observed to decrease slightly with increasing proportions of sulphur.

TABLE LI

Corn Oil + Sulphur + P.P. at 140°C.

Expt. No.	Sulphur %	P.P. %	Time (Min.)
224	15		600 (not gelled)
225	20		392
226	23		349
227	30		287
228	35		274
229	20	2	311
230	23	2	227
231	26	2	223
232	30	2	190
233	35	2	174
234	40	2	161

Attention was now turned to semi-drying oils in order to see how they would react with sulphur. Corn oil requires an excess of sulphur in order to gel comparatively quickly, and as found in the case of linseed oil the greater the excess the shorter the time of setting. The rate of sulphur combination was observed to be much slower than with linseed oil, and the long time required for gelation to occur was partly due to that. The formation of acetone-insoluble material also proceeded slowly.

P.P. produces almost the same absolute amount of decrease in the time of setting of corn oil as it does in linseed oil, namely about 80 to 90 minutes.

The product obtained at gelation is quite similar to that produced by linseed oil with the same quantity of sulphur.

TABLE LII

Perilla oil + 20% Sulphur + P.P. at 140°C.

Expt. No.	% P.P.	Time (Min.)
235		189
235	2	119

Perilla oil, another good drying oil, was found to give results that were quite comparable with those obtained in the case of linseed oil. A very tacky product was obtained at gelation both with and without the accelerator.

TABLE LIII

** China wood oil + Sulphur + Various Accelerators at 140°C.

Expt.No.	Sulphur %	Accelerator %	Time (Min.)
237	15	2% P.P.	15
238	20	2% P.P.	11.5
239	17	2% P.P.	11
240	17	1%P.P.	17
241	17	2% Captax	67
242	17	2% Grasselli 808	13
243	17	2% Aldehyde-ammonia	14.5
244	17	2% Diphenylguanidine	17
245	17	2% P-nitrosodimethylaniline	16.5
246	17	2% Tetramethylthiuramdisulphide	19.5
247	17	2% Hexamethylenetetramine	40.5

** Fresh Oil

Only a slight difference is noticed in the effect of several of the accelerators, and their action is found to be quite pronounced as in the case of rubber. Hexamethylenetetramine is only found to show a moderate effect, but this was observed to be due to the slow rate of sulphur combination.

As soon as a dark cherry red color formed the actual gelation occurred quickly just as it does with P.P. Captax did not produce an acceleration at all. In the case of Grasselli 808 the material was on the point of setting in 12 or 13 minutes, but it remained in that state for an additional 12 minutes whereas with the other accelerators it takes only a minute or two.

TABLE LIV

Linseed oil + China wood oil + 25% Sulphur +P.P. at 140°C.

Expt. No.	Linseed oil %	China wood oil %	P.P. %	Time (Min.)
248	90	10		137
249	90	10	2	74
250	75	25		112
251	75	25	2	57

In the above experiments China wood oil was added to linseed oil in order to see whether small increases in the quantity of the easily-polymerisable material would hasten the setting of linseed oil. By comparison with experiments #208 and #210 it is seen that an appreciable decrease in the time of gelation was obtained.

EXPERIMENT 252

The ether-soluble material prepared in experiment #118 was mixed with its own volume of chloroform, and about

10 per cent. of its weight of $SbCl_5$ added (a 10 per cent. solution of $SbCl_5$ in chloroform was used). The material was found to gel immediately in the cold, the heat of reaction driving off a great deal of the chloroform. The same result was obtained with $SnCl_4$ when it was used instead of $SbCl_5$.

When the $SnCl_4$ solution was added to China wood oil (the oil is partially oxidised as it only requires a little over 12 per cent. of sulphur in order to give optimum results) gelation again occurred immediately in the cold. Raw linseed oil treated in the same way did not show any signs of thickening.

A determination of the quantity of acetone-insoluble and ether-insoluble material present at gelation in the above are noted in the following table. A correction was made for the quantity of $SbCl_5$ or $SnCl_4$ used, but the results may be taken as only approximate.

TABLE LV

%Acetone-insoluble			% Ether-insoluble		
$SbCl_5$	$SnCl_4$	$SnCl_4$ on China wood oil	$SbCl_5$	$SnCl_4$	$SnCl_4$ on China wood oil
55.4	54.0	60.6	57.3	57.0	68.4

The quantity of acetone-insoluble material present at gelation in the above experiment is of the same magnitude as that obtained ordinarily at high temperatures, but the amount of ether-insoluble material is greater. Hence the products obtained above may represent a more advanced state of the gelation process. This is probably the case as the products obtained are brittle and can be rubbed to a powder, and a similar brittle (although softer) material is generally obtained on continued heating of the sulphurised oil for a long time after gelation, as in experiment #120.

Since $Sn\ Cl_4$ and $Sb\ Cl_5$ are well-known polymerising agents, it appears likely that some polymerisation does occur on heating oil and sulphur at high temperatures. This will be discussed later.

EXPERIMENT 253

Crotonaldehyde was heated with one and with two gram atoms of sulphur both with and without 2% P.P. on a boiling water bath, a long reflux tube being attached to each test-tube. The samples containing the accelerator showed a much more rapid rate of sulphur combination, being as far advanced in three hours as the control samples were in twelve as regards combination of the sulphur. No evidence of thickening was apparent.

When the P.P. was added to the crotonaldehyde there was an immediate change in color indicating a reaction between the two.

DISCUSSION OF RESULTS

Since most of the work in this investigation was carried out with linseed oil, only the results obtained with this oil will be discussed. A note will be made at the end of any differences between this and other oils.

The results obtained during the course of the work indicate that the sulphurisation process consists of five stages: solution of the sulphur, combination of the sulphur, the formation of a liquid intermediate acetone-insoluble fraction, the formation of a solid ether-insoluble fraction, and finally gelation. None of these stages is separated by well-defined boundaries from the others. Solution and combination of the sulphur proceed concurrently, acetone-insoluble material begins to form as soon as a definite quantity of sulphur has combined, ether-insoluble material forms after about 48 per cent. of acetone-insoluble material is present, and gelation occurs when there is a sufficient quantity of the former. After the setting the amount of acetone-insoluble and ether-insoluble material increases with prolonged heating.

The temperature and the percentage of sulphur were observed to be the two main factors in the whole process. Combination of the sulphur is very slow at low temperatures, but very rapid at, say, 160°C. As soon as a definite quantity of sulphur is combined the formation of acetone-insoluble material takes place quickly at the start, even at low temperatures, but its rate of formation increases with the temperature and depends, furthermore, upon the quantity of combined sulphur present. This in turn depends on the proportion of sulphur used. After a time the rate of formation of this acetone-insoluble material slows up, and when about 48 per cent. has been produced ether-insoluble material forms very rapidly. Gelation occurs when a definite amount is present, the quantity depending on the temperature, the percentage of sulphur, and the proportions of other materials added. Continued heating after setting produces an increase in the quantity of acetone-insoluble and ether-insoluble material, and to this fact may be due the change from a tacky, elastic product at gelation to a non-tacky and non-elastic one.

Judging by molecular weight determinations the acetone-insoluble material appears to be at least bimolecular, and since no appreciable variation in the molecular weights occurred on varying the concentration, polymerisation may be considered as having occurred.

On the other hand, the formation of the ether-insoluble material appears to be a colloidal phenomenon in which the polymerised acetone-insoluble material has aggregated. The fact that it forms so quickly after 48 per cent. of acetone-insoluble material is present, that gelation depends on its presence, that the amount necessary varies with the temperature and the materials added, and that the quantity increases markedly on prolonged heating after gelation indicates that colloidal changes are at the root of the setting. Continued heating after gelation causes the sulphurised oil to become partly insoluble in benzene, thus showing that larger aggregates are being formed.

Now turning to the effect of added materials, such as accelerators, it was found that most of the accelerators used appeared to have a very narrow range of maximum effectiveness, whereas the others have a slightly greater range. 130 to 140°C. seems to be the optimum temperature for most of the accelerators examined, a higher temperature, say 160°C., producing a retardation instead of an acceleration. Since the rate of sulphur combination does not seem to be affected, this must be due to a dispersive effect of the accelerator or its decomposition products which slows up the formation of both the acetone-insoluble and ether-insoluble material, especially the latter. P.P., the zinc salt of the linseed oil fatty acids plus one equivalent of piperidine, and a combination of isopropyl dixanthogen and zinc isopropyl xanthate plus one equivalent of piperidine produced an acceleration at 160°C.

At any temperature the same quantity of different accelerators, when used alone, produce the same amount of acetone-insoluble material at gelation, but they show variations in its rate of formation. P.P. and zinc P. decompose during the reaction as a white sublimate forms at the top of the tube, and it begins to form much more quickly at higher temperatures indicating that they act more quickly then. The quantity of white sublimate increases for some time showing that the action of the accelerator is not instantaneous. The white sublimate is considered to be a carbonate of piperidine as it does not form if the carbon dioxide is excluded.

An optimum quantity of accelerator appears to be necessary in order to get the shortest time of setting, because a large amount exerts a twofold action. It first markedly increases the rate of sulphur combination, and then exerts a dispersive effect which retards the formation of the large aggregates essential for gelation. Hence if the optimum quantity was used the increase in the rate of sulphur combination would overshadow, to the greatest extent, the effect of the dispersive action. In most cases the decomposition products exert a greater peptising action than the accelerator itself, and since the difference in the quantity of acetone-insoluble material at gelation between the sample containing an accelerator and the control is more marked at higher temperatures, more must decompose.

Two per cent. of the zinc salts of the dithiocarbamic acids plus one equivalent of piperidine, although not giving as good results as 5 per cent., is still the most economical proportion to use. However it must not be considered the optimum amount.

Zinc oxide was found to enhance the action of P.P., isopropyl dixanthogen and monoxanthogen, and captax, but the activation was not very great. In the case of P. P. an optimum amount, 1 per cent., was observed to give the best results when 2 per cent. of the accelerator was present, smaller or larger proportions (except within narrow limits) producing a retardation which was greater at lower temperatures. The activation seems to be due almost entirely to an increased rate of sulphur combination. Having too much zinc oxide present also produces an initial increase in the combination of the sulphur (not as much as when the optimum amount is used), but later it exerts a dispersive action which overshadows the initial activation, and hence the time of setting is increased.

5 per cent. of zinc oxide was shown to enhance the action of captax. Consequently every accelerator may not require the same optimum proportion and may not be so sensitive to variations. Also the action of each accelerator is not enhanced to the same extent, isopropyl dixanthogen being activated the most. In the case of the zinc dithiocarbamates the optimum proportion of zinc oxide was not found, all proportions used giving a retardation.

Mixing the sulphur with the accelerator or with zinc oxide retards their effect. Consequently it appears that the accelerator must exert its effect on the oil, and mixing it with sulphur perhaps enables it to be decomposed before it can exert its influence.

Large amounts of zinc give the material a brown or reddish-brown colour whether present as zinc oxide or as the zinc salt of a dithiocarbamic acid.

Driers such as manganese oxide and manganese resinate produce a retardation when used alone. With P.P. manganese oxide shows no affect whatever, but the resinate produces the same initial activation as zinc oxide as regards the sulphur combination. However it later exerts a dispersive effect which greatly increases the quantity of acetone-insoluble material at gelation. When the resinate is used both alone and with P.P. the material for some time after setting is very elastic, quite rubbery, and practically non-tacky, these characteristics being more noticeable when the accelerator is present.

In the presence of an accelerator, piperidine only shows an activation when it can react with a zinc salt or form an addition compound as with the zinc salts of the accelerators and captax respectively. One equivalent of the base is the optimum quantity, less than that amount not being as detrimental as more. The effect of an excess or a deficit is chiefly to decrease the rate of sulphur combination. Piperidine alone produces an acceleration quite comparable with that shown by the same quantity of P.P.

At 140°C. aniline and dibenzylamine decrease the solubility of the sulphur tremendously, and thus there is a marked reduction in the rate of sulphur combination. This is verified by the fact that a polymerising agent such as zinc chloride aniline had a negligible effect when added after the sulphur was all combined. At 160°C. dibenzylamine did not affect the combination of the sulphur but did exert a great dispersive action. Piperidine was also found to decrease the solubility of the sulphur, except in those cases where it enhances the action of the accelerator, as no sulphur separated out from any of the samples containing it even when only a trace of acetone-insoluble material had formed.

The zinc salt of the linseed oil fatty acids plus one equivalent of piperidine is quite a good accelerator, but again there is an optimum quantity to give the best results. In this case it is about 3.5 per cent. Less zinc is required when it is in the form of soluble zinc salt than as zinc oxide in order to give the best results. When used with 2 per cent. of P.P. between 1 to 2 per cent. of the above zinc salt will enhance the action of the accelerator to the greatest extent, that is, have the largest difference between its initial activation and its final dispersive action. Piperidine has only a slight effect in this case, even when present in excess.

Thus it is seen that a combination of accelerators give better results than each accelerator alone, the increased effect being exerted chiefly at the beginning.

In those cases where piperidine markedly enhances the action of the accelerator as in zinc isopropyl xanthate, permitting the material to stand overnight causes a decrease in the effectiveness, whereas with the zinc salt of the linseed oil fatty acids no reduction was noticed. This is considered due either to an escape of piperidine or to a reaction between it and the zinc isopropyl xanthate.

It was found that low percentages of sulphur will produce gelation if heated at a sufficiently high temperature. With 8 per cent. gelation occurred at 180°C., and 6 per cent. would have caused setting if the material had been heated long enough. At that temperature the decomposition products of accelerators exert a marked retardation. This material has very little bulk at gelation, but it becomes denser on continued heating. However it is still extremely tacky after two hours.

All the evidence so far points to the fact that the combination of the sulphur is a time reaction, the rate increasing with the temperature, the amount of accelerator, and to a lesser extent with the proportion of sulphur. Using 16 per cent. of sulphur at 140°C. a sample containing 2 per cent. of P.P. has as much sulphur combined in 83 minutes as the control in an hour longer, but the difference in the time of gelation was over one hour and a half. Also with 20 per cent. of sulphur it remained in solution 95 minutes longer without the accelerator. Hence the accelerator appers to have a twofold function as it increases both the rate of combination of the sulphur and the later stages of the process, the former being the more important. At 160°C. the second function may be almost negligible.

That the accelerator does not aid the solution of the sulphur seems to be best indicated by isopropyl dixanthogen. This accelerator exerts a powerful action in the case of rubber, but shows its effect only over a narrow range of temperature from 110 to 125°C. With oils, however, it is only slightly effective at that temperature, and as solution of the sulphur is very slow at 116°C. the reason for its ineffectiveness is apparent.

The same accelerator has no effect at all when used with rubber at 140°C., but with oils it gives quite good results. Hence this is evidence of differences in the effect of accelerators in the presence of oils and rubber.

Any activation of an accelerator, either by the use of zinc oxide or piperidine or the presence of a combination of accelerators, seems to show its action mainly in an increased rate of sulphur combination. It is a striking fact that at any temperature, using a definite percentage of sulphur and approximately equivalent quantities of several accelerators, there is a limit to the amount of reduction attainable in the time of gelation, even with activation, and no further decrease can be obtained by using a combination of them.

Of the uncombined sulphur present during the sulphurisation at 140°C., there is always more of the sulphur undissolved than dissolved when the accelerator is present, whereas the reverse holds true in its absence. Hence this further shows that the solution of the sulphur is the slow process, and that the accelerator does not aid it directly. It does so indirectly by causing the sulphur to combine more quickly and thus destroying the equilibrium constantly.

Contrary to what was noticed at 140° C., very little dissolved sulphur is present at 160°C. after 45 minutes even though there is a considerable quantity of undissolved sulphur. Hence it seems that at 160°C. combination of the sulphur takes place as soon as it dissolves, and that the dissolving of the sulphur is the slow process even at that temperature. Using 14 per cent. of sulphur at 160°C. practically all the sulphur is combined in 80 minutes, whereas Chataway (1) found that it took less than 45 minutes. Considering that she obtained this result by finding no ether-insoluble material present after 45 minutes and not by removing the tube from the bath, the reason for her erroneous conclusion is apparent.

Besides cutting down the time of gelation as already noted the accelerators also improve the material at gelation by making it denser, less tacky, and more elastic. The speed with which the actual setting takes place, after the material seems to be on the point of gelation, varies with the material added, their proportions, and the temperature. As a rule the higher the temperature the sharper is the end-point. At 140° C, the material may remain tacky for over half an hour after gelation, whereas at 160°C., in the presence of an accelerator, it becomes non-tacky and brittle in about ten minutes. At the lower temperature it seems to be more spongy and rubbery.

A rise of 10°C. was found to reduce the time of gelation by about a third or one-half with and without the presence of an accelerator, and the quantity of acetone-insoluble material at gelation increased somewhat with the temperature only when an accelerator was present. Regardless of the temperature, the proportion of sulphur, or the amount of added materials, over 50 per cent. of acetone-insoluble material must be present before gelation occurs. It must be remembered that this statement only applies when 20 times its weight of acetone is used for extraction.

There is a great decrease in the time of setting with increasing proportions of sulphur. The quantity of acetone-insoluble material at gelation increases slightly up to 18 per cent. of sulphur, and then rises more sharply. A very marked increase in the amount of acetone-insoluble material formed at the end of 30 minutes was observed when 18 and 20% sulphur were used in the presence of an accelerator, and the same thing might apply without it at a longer period of time. The quantity of acetone-insoluble material formed by the time no free sulphur remains depends on the proportion of sulphur used.

Adding an accelerator after no dissolved sulphur is present but while some is still undissolved causes a tremendous change in the appearance of the material, as it becomes extremely bulky within a few minutes and looks like the control sample near gelation. The quantity of acetone-insoluble material at the setting-point was markedly increased thereby. Only a small decrease in the time of setting was obtained, but this is due to the slow rate at which gelation occurred and the production of a very indeterminate end-point. It appears that a smaller amount of accelerator would have given better results. When the accelerator was added after the sulphur was all dissolved and combined the same changes took place as described above, a decrease of one-third in the time of gelation from this point being obtained. This time, however, the initial change in density was not so marked as only 14 per cent. of sulphur was used, and a lower proportion of sulphur always gives a less bulky material.

Since the above experiments tended to prove that the accelerator did aid the later stages of the sulphurisation process there was always the possibility that some uncombined sulphur may have been present, and this would have tended to affect the result. Consequently a number of experiements were performed in which the sulphurised oil was extracted with dried ether, the ether evaporated in vacuo, and P.P. added to portions of this material with heating. The results indicated that the accelerator markedly increased the rate of formation of the ether-insoluble material provided that the acetone-insoluble material had been formed during a long period of heating, and only a slight variation in its rate of formation was found to occur on varying the temperature in the presence of an accelerator. Without the accelerator the rate doubled for a rise of 10 degrees.

When the linseed oil was heated with a large excess of sulphur at 160°C. for a short time in order to cut down the time of heating of the sulphurised oil, and the material then extracted with ether, it was found that the accelerator did not affect the setting of the sulphurised oil appreciably, regardless of the temperature.

The acetone-soluble fraction of sulphurised linseed oil was observed to set on heating for a long period of time, but the presence of P.P. caused a marked retarding effect. Hence it seems likely that prolonged heating of the sulphurised oil enables sufficient change in the acetone-soluble material to take place to permit the accelerator to show its effect in increasing the rate of formation of the ether-insoluble material. The acetone-soluble material was shown to be the factor which slows up the setting of linseed oil.

The accelerator does not seem to produce any positive increase in the rate of formation of the acetone-insoluble material, although indirectly it does do so as its rate of formation depends on the percentage of combined sulphur, and the rate of sulphur combination is greatly increased by an accelerator.

The sulphurisation of china wood oil was found to vary considerably from that of linseed oil . Without an accelerator china wood oil, with an excess of sulphur, gelled in about half the time required for an excess of sulphur to produce gelation in the case of linseed oil, and it was not so subject to variations in the proportion of sulphur. Whereas the effect of accelerators and their activators was evident in the case of linseed oil regardless of whether an excess or a deficit of sulphur was employed, the same condition did not hold in china wood oil. With an excess of sulphur the latter gave almost identical results with those found for linseed oil, except that the accelerators showed a much greater effect with china wood oil (quite comparable with that found in rubber) and did not vary much with the temperature. However, with a deficit of sulphur, only one example of appreciable acceleration was found. China wood oil required a smaller quantity of acetone-insoluble material to be present before gelation occurred, but even then the amount was in the neighborhood of 50 per cent.

A drying oil such as perilla oil gave results that were quite comparable with those obtained using linseed oil, as did also a semi-drying oil such as corn oil, but it was observed that in the latter case the rate of sulphur combination was slower, and hence a longer time was required for gelation.

Stannic chloride and antimony pentachloride, which are well known polymerising agents, caused sulphurised linseed oil (formed on prolonged heating at 140°C. and containing 20% of sulphur) and slightly oxidised china wood oil to gel immediately in the cold yielding a material which was comparable to that obtained at high temperatures by heating for a long time after gelation. This would enhance the idea that polymerisation takes place.

Although thickening did not occur , P.P. was observed to produce a marked acceleration in the rate of combination of crotonaldehyde and sulphur.

It is believed that evidence was obtained to ~~slow~~ show that sulphurised linseed oil had a two-phase composition. Oxidised linseed oil was shown by Eibner and Greth (71) to also have a two-phase composition which could be separated by formic acid.

It has also been found that different samples of linseed oil gave a differnt time for gelation, indicating differences in their composition. Slansky (26) observed this same feature during the oxidation process.

Most investigators are agreed that the mechanism of the drying of oils under the influence of air and the thickening or setting of oils under the influence of heat are analogous, and Whitby and Chataway (1) believe that they both appear be similar to the setting of oils under the influence of sulphur and heat. In all cases an intermediate liquid fraction insoluble in acetone but soluble in ether is first formed, then a solid fraction insoluble in ether forms, and finally the viscosity of the material increases very rapidly from this point to the setting. Slansky (26) found that when 40 per cent. of oxy-acids had formed in oxidised linseed oil the material became solid and was partly insoluble in ether. In the sulphurisation process about 30 to 40 per cent. of ether-insoluble material had to be present before gelation occurs, the amount varying with the materials added and the temperature.

Molecular weight determinations of the acetone-insoluble material from sulphurised linseed oil indicate that it is a bimolecular compound. Only a few investigators are opposed to that view in the case of the blowing and boiling of oils. Colloidal changes are generally assumed to be be responsible for the actual setting of the acetone-insoluble material, and indications are that the same thing applies in the sulphurisation process.

Turning now to a comparison of the sulphurisation of oils and the vulcanisation of rubber it is found that the main chemical change which takes place is the addition of sulphur at some of the double bonds. In both cases this causes a marked change in the physical proporties. The oil becomes more viscous and finally sets to a gel, which in some cases may be somewhat elastic and only slightly tacky, while the rubber shows a great increase in its elasticity, tensile strength, and ageing properties. The rate and the amount of these changes depend on the proportion of sulphur and the temperature.

The use of organic accelerators causes not only a great shortening in the time of vulcanisation of rubber but also a tremendous improvement in the physical properties, especially as regards ageing. These improved characteristics are considered due to the lower content of sulphur capable of being used, the lower temperature possible, and the shorter time of heating, and so the effect of the accelerator is indirect instead of direct, With oils, as with rubber, the presence of the accelerator generally necessitates the use of a low temperature, say 140°C., in order to get the best results. Also, in both cases, some of the accelerators produce their effect over a wide range of temperature whereas others do so only over a very narrow range, and variations are found in their relative effectiveness. However, the decrease in the time of heating and the improvement in the physical properties which they produce are not nearly as great in linseed oil as in rubber, although the material does become denser, more elastic, and less tacky at gelation. China wood oil, with an excess of sulphur, gives results comparable to those of rubber as regards the reduction in the time of setting and the non-tackiness of the material.

The addition of zinc oxide, bases, etc., is known to enhance the action of many organic accelerators when used in rubber. The same thing, with limitations, has been found to hold in oils, although, as before, the activation is not nearly as great in the latter.

Both in the case of the sulphurisation of oils and the vulcanisation of rubber the presence of the accelerator, either with or without its activator, markedly increased the rate of combination of the sulphur, but whereas in the case of rubber the rate increased with increasing proportions of accelerator, an optimum proportion was found to give the best results in linseed oil. The effect of the accelerators on the changes which take place after the sulphur combines is not very apparent in the case of oils except that it makes the sample containing the accelerator appear denser, whereas with rubber we have a great improvement in the physical proporties.

That there should be differences in the effect of accelerators and their activators in the two processes is quite understandable, as on the one hand we start with a very fluid oil and on the other we have a material which is already in a high state of aggregation.

As to the mode of action of the accelerators, most authors consider that they do not exert their effect directly upon the rubber, but act on the sulphur and change it into a more active modification capable of reacting more quickly with the rubber. Various theories have been put forth by Dubosc (72) Ostromysslensky (73), Kratz (74), Bruni and Romani (75), Scott and Bedford (76), Twiss (77), and others for the action of any one class of accelerators, but most of them have exceptions or are in opposition to other theories. The main trend, however, is the initial formation of addition or reaction products between the sulphur and the accelerator, and the consequent decomposition of these give an activated form of sulphur which they consider to be the true vulcanisation accelerator. Most of the investigators say it is thio-ozone (S_3), while Bedford and Sebrell (78) even claim it is trithio-ozone. The enhanced activity given to the organic accelerators, which may form addition products such as polysulphides, by the presence of zinc oxide, lead oxide, etc., is considered due to the decomposition of the addition products by the zinc oxide.

Recently, Whitby and Cambron (79) introduced a new view-point into the theories of accelerator action by suggesting that their action is not due to the activation of the sulphur but to an effect on the rubber itself. They consider that the presence or the formation of soaps during the vulcanisation produces an increased dispersion of the rubber. This causes a greater reactivity in the latter, thereby making it combine with sulphur more quickly.

The results obtained during the sulphurisation of oils does not seem to throw any further light on the mode of action of the accelerators.

Tackiness

The sulphurisation of linseed oil at a temperature of 140°C. instead of 160°C. using the same percentage of sulphur, say 16 per cent., gives a less tacky, denser, and more elastic material at gelation. However it takes much longer for the tackiness to disappear at the lower temperature, and the material has compressible elasticity for a large part of this time. Increase in the proportion of sulphur also decreases the tackiness at gelation, and it does not take as long for the tackiness to disappear. Using 8 and 12 per cent. of sulphur at 180°C. setting takes place, very quickly in the latter case, but the material is extremely tacky even three hours after gelation and has little bulk.

In the presence of the accelerators at 140°C. a much denser material is obtained, and it has more compressible elasticity and is much less tacky. The addition of manganese resinate greatly enhances these features and, in addition, the material assumes extensible elasticity.

Now it was found that the accelerators increased the quantity of acetone-insoluble and ether-insoluble material at gelation, and that continued heating after gelation both with and without an accelerator increased the quantity of each, especially the latter, and also caused the formation of larger aggregates which were insoluble in benzene. During the additional heating the material became non-tacky and could be rubbed to a soft powder.

In determinating the acetone-insoluble material it was observed, towards the end of the extraction, that the acetone-insoluble material consisted of solid particles ~~of~~ if it contained a large proportion of ether-insoluble material, that it was a very spongy tacky gel if it contained only a small proportion, and that it was a very viscous fluid if the ether-inslouble material had not started to form. Also, even if a large proportion of ether-insoluble material was present, extraction with acetone caused it to pass through a stage in which it was a very tacky spongy gel which, on further extraction, became solid particles.

Consequently it appears that the disappearance of the tackiness and elasticity depends on the aggregation of the acetone-insoluble material to form ether-insoluble material, and then further aggregation to form benzene-insoluble material. Hence a material to be elastic must contain a proper proportion of a solid disperse phase and a liquid dispersion medium.

SUMMARY

The sulphurisation of oils has ~~oils has~~ been shown to consist of five stages: solution of the sulphur, combination of the sulphur, the formation of a liquid intermediate acetone-insoluble fraction, the formation of a solid ether-insoluble fraction, and finally gelation. None of these stages were found to be separated by well-defined boundaries from the others. Solution and combination of the sulphur proceed concurrently, acetone-insoluble material begins to form as soon as a definite quantity of sulphur has combined, ether-insoluble material forms when about 48 per cent. of acetone-insoluble material is present (empirical value), and gelation occurs when there is a definite amount of the former.

The rate at which these stages proceed was found to vary with the temperature, the percentage of sulphur, and the nature and amount of added materials such as organic accelerators, zinc oxide, bases, and driers.

Molecular weight determinations indicate that the formation of acetone-insoluble material is due to polymerisation, but that the formation of ether-insoluble material and the actual setting are due to colloidal changes. However this cannot be considered as definitely settled.

Linseed and china wood oils were shown to respond similarly to the effect of organic accelerators and their activators, provided that an excess of sulphur was present with the china wood oil, but the relative acceleration produced was much greater in the latter and is quite comparable with that obtained with rubber. With a deficit of sulphur china wood oil showed an appreciable acceleration in the time of setting in only one instance, although the rate of sulphur combination was markedly increased in most cases.

In the sulphurisation of oils organic accelerators were found to produce a marked increase in the rate of sulphur combination and in the rate of formation of the ether-insoluble material, and not to affect the rate of formation of the acetone-insoluble material. With rubber they are known to produce an increased rate of sulphur combination, and a tremendous improvement in its tensile strength, elasticity, and ageing properties. Variations in the relative effect of various accelerators with oils, were found, and similar variations occur with rubber.

Tackiness was shown to be due to the presence of a relatively large proportion of the viscous liquid acetone-insoluble material as compared to the solid ether-insoluble material.

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