CCCLXIX.—*A Study in the Formation of Gels. Vulcanised Oils.*

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It has been shown (Stamberger, *Rec. trav. chim.*, 1927, **46**, 837; 1928, **47**, Oct. 15) that an insoluble, tough, elastic substance is formed by heating triolein with sulphur. The process may be divided into three stages: (1) Combination of the triolein with sulphur; (2) polymerisation of these molecules to double molecules; (3) further polymerisation giving the elastic substance. From the reaction mixture may be separated an acetone-soluble portion corresponding to stage 1, and a benzene-soluble portion (stage 2). The remaining highly polymerised product is insoluble.

Further information has now been obtained on the processes concerned by two methods: (*a*) *X*-ray examination of the products; (*b*) examination of the behaviour of the soluble products when spread as thin films on a water surface.

EXPERIMENTAL.

For convenience the details of the various products which have been examined are given in Table I.

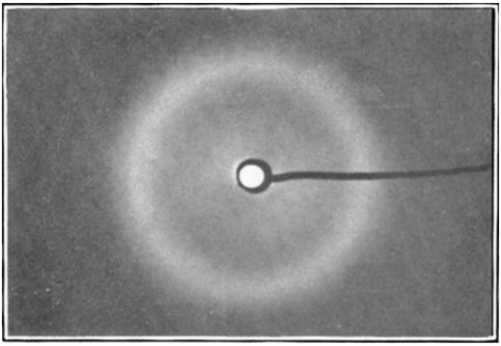
TABLE I.

Substance.	*d.*	Sulphur content, %.	No. of S atoms per mol.	State of aggregation.	*M*, calc.	Diameter of circle in *X*-ray diagram.
Triolein.	0·920	—	—	Liquid.	884	28·06 mm.
Vulcanised triolein:						
Acetone-soluble.	1·03	16·6	4— 5	Very viscous liquid.	1044 1076	27·74
Benzene-soluble, I.	1·04	16·4	10—12	Viscous, pasty liquid.	2088 2152	27·68
Benzene-soluble, II.	1·04	16·4	10—12	Slightly elastic, sticky solid.	2088 2152	28·10
Benzene-soluble, III, dissolved by heating not higher than 60°.	—	16·4	—	More elastic than I and II.	7000 (cryoscopic)	—
Insoluble, elastic solid.	—	16·3	—	Tough, elastic substance.	—	28·10
Oleic acid.	0·891	—	—	Oil.	282	—
Fatty acids from saponification of vulcanised triolein.	0·971	13·7	3— 4	Very viscous liquid.	937 969	— —

The *X*-ray diagrams were obtained by the method described by Katz (*Z. Physik*, 1927, **45**, 100) with Cuα rays. All the products gave circles of the same diameter (Figs. 1*a* and *b*), which is calculated for a distance of 40 mm. between the substance and the photographic plate, and shown in Table I; these circles indicate an amorphous structure. The *X*-ray examination did not show any change in the molecules in the different stages of the reaction.

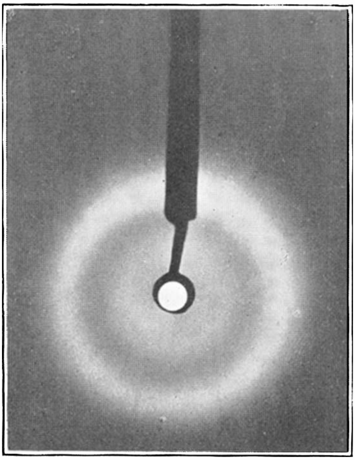
Unimolecular Films.—The soluble products and the sulphur-containing oleic acid obtained by cold saponification have been found to give unimolecular films of the expanded type when spread on water. The films of these substances have been studied by using the apparatus and technique of Adam (*Proc. Roy. Soc.*, 1926, *A*, **110**, 423). Dilute benzene solutions of known concentration of the several products were prepared. Known weights of these solutions were placed upon a clean water surface in a Langmuir–Adam trough by means of a capillary drop-pipette. The force of compression acting on the film when the area was diminished was measured by means of Adam's torsion apparatus (*loc. cit.*).

The results of the measurements are given in Figs. 2 and 3, where the compressing force (*F* in dynes/cm.) is plotted against the thickness of the film (in Ångström units). The molecular weights of the substances cannot be accurately determined, as they are not sharply defined chemical compounds. We have preferred, therefore, to plot the thickness of the film as calculated from its area, the weight of substance, and its specific gravity (*d* in Table I), rather than the area per molecule. In Table II are collected the values for the dimensions of the molecules derived



X-*Ray diagram of triolein.*

FIG. 1*a*.



X-*Ray diagram of vulcanised triolein.*

FIG. 1*b*.

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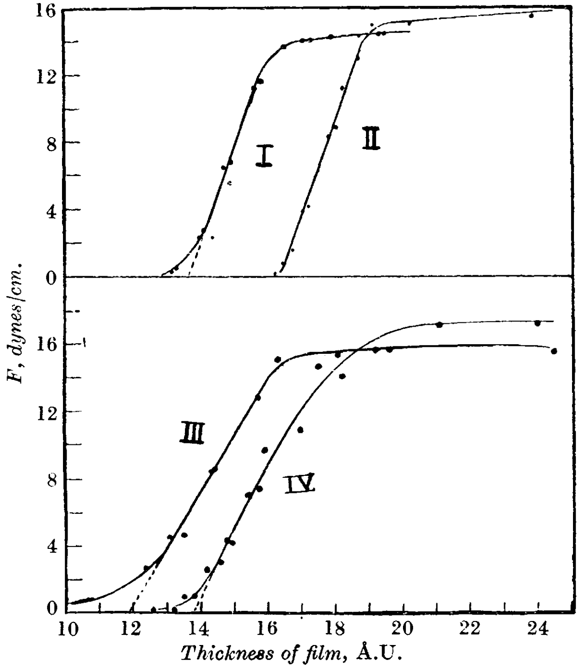
from the curves. The areas per molecule have been calculated approximately, assuming theoretical molecular weights derived from the sulphur content and the cryoscopic measurements.

FIG. 2.



Curve *I. Benzene-soluble part, I and II,* 16°.
,, *II. Benzene-soluble part, III,* 18°.
,, *III. Triolein.*
,, *IV. Acetone-soluble part,* 16°.

TABLE II.

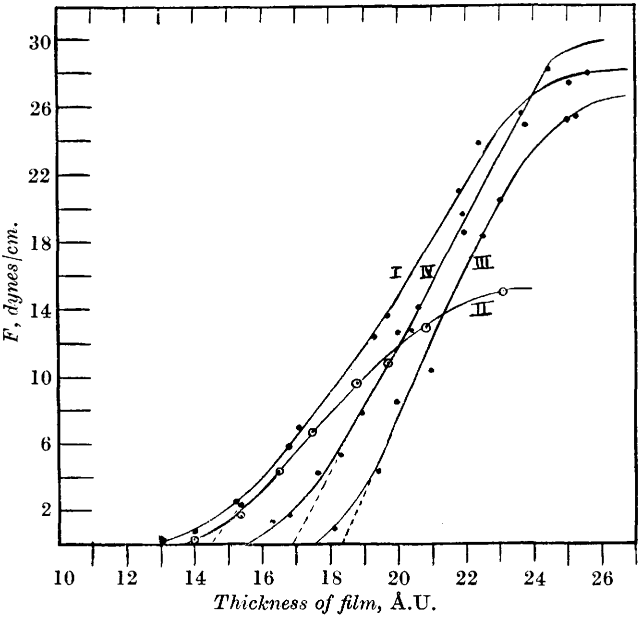
Substance.	Thickness in film at zero pressure.	Temp.	Area per molecule, sq. Å.U., at zero pressure.
Triolein	13·0 Å.U.	16°	132
Acetone-sol.	13·9	16	125
Benzene-sol., I and II	13·9	16	260
Benzene-sol., III	16·3	18	—
Oleic acid	13·8	16 and 1	35
Sulphurised oleic acid	16·9	16	96
Sulphurised oleic acid	18·5	1	86

Discussion.

It is of interest to correlate the observations made in the above experiments with the physical properties of these substances and with the appearance of elastic properties.

The combination with sulphur in the first part of the reaction does not alter the mode of orientation, and only very slightly affects the dimensions of the molecule. The film of the acetone-soluble product is about 1 Å.U. thicker at zero pressure than that of triolein, indicating that the hydrocarbon chains are tending to be oriented more nearly perpendicular to the water surface. The position of the sulphur in the molecule is not definitely determined. Most probably it is in a chain connecting the double bonds of the adjacent oleic acid chains, since after saponification most of the sulphur is still attached to the fatty acids. About 16·5% of the sulphur is found with the glycerol after saponification, not as inorganic sulphur. Cryoscopic determinations on these sulphur-containing fatty acids show that they are still combined in groups of three. The acetone-soluble product of the first stage of the reaction is a viscous fluid substance having no elastic properties.

FIG. 3.



Curve I. Oleic acid at 1°.
,, *II. Oleic acid at* 16°.
,, *III. Sulphurised oleic acid at* 1°.
,, *IV. Sulphurised oleic acid at* 16°.

In the second stage of the reaction the molecules polymerise first to double molecules. This is the benzene-soluble part, and is a viscous, pasty fluid substance, slightly elastic. This substance changed to a still more elastic sticky solid on standing for 3—4 months in a closed weighing bottle. This change could be accelerated by heating or by irradiation with ultra-violet light. An elastic solid was also obtained by keeping the benzene-soluble part under water or acetone for several days. These solid products only swelled in benzene at room temperature, but could be dissolved on continued boiling. It appears probable that the highly polymerised or aggregated molecules of the elastic solid obtained from the benzene-soluble part in this manner had been broken down by the hot solvent to double molecules. All these benzene-soluble products gave the same results on spreading on water. The thickness of the film was about the same as that of the acetone-soluble part. The area per molecule at zero pressure, calculated from the theoretical molecular weight (cryoscopic measurements and sulphur content), was twice that of the acetone-soluble part. This indicates that the double molecules are formed by the joining of two molecules side by side. The polar glyceryl groups are apparently unaltered, since the orientation is unaffected.

By careful heating with benzene for 2 days at a temperature not higher than 60°, the elastic polymerised product obtained from the benzene-soluble part (I) (by standing for 3—4 months at room temperature) could be completely dissolved. Cryoscopic measurement showed a very high molecular weight, at least 7000. This product (benzene-soluble, III) gave, on spreading, a film 16·3 Å.U. thick—again a unimolecular film. The slightly greater thickness of this film may be due to the polymerisation to larger groups of molecules (at least 7) causing closer packing of the fatty-acid chains. The form of the compression curve at low pressures shows that the film is there much less expanded (see Fig. 2).

The same elastic polymerised product was nearly completely dissolved on being kept under benzene at room temperature for 14 days. This solution gave no freezing-point depression even at a concentration of 7%. Accurate figures for the film thickness cannot be given owing to traces of substance being undissolved. Several measurements gave values for the thickness of 17 Å.U. at zero pressure, showing at least that the film is still one molecule thick. These measurements show that the higher molecular aggregates are formed by the linking of several molecules side by side, repeating the method of formation of the double molecules.

After saponification the elastic properties of the solid disappear. The sulphurised oleic acid is a viscous liquid. Moreover, no elastic substance could be obtained by heating oleic acid with sulphur. The sulphurised acids obtained by both methods gave films of the same thickness, a little thicker than oleic acid. Since the fatty acids are in groups of three after saponification of both the benzene-soluble part and the elastic solid (see Stamberger, *loc. cit.*), it seems that the polymerisation is not caused by sulphur linking together hydrocarbon chains of adjacent molecules, but rather suggests that the glyceryl portion of the molecules takes part in the combination to give the elastic solid. If this is broken by saponification, the elastic properties disappear, although the fatty acids are still held together in groups of three.

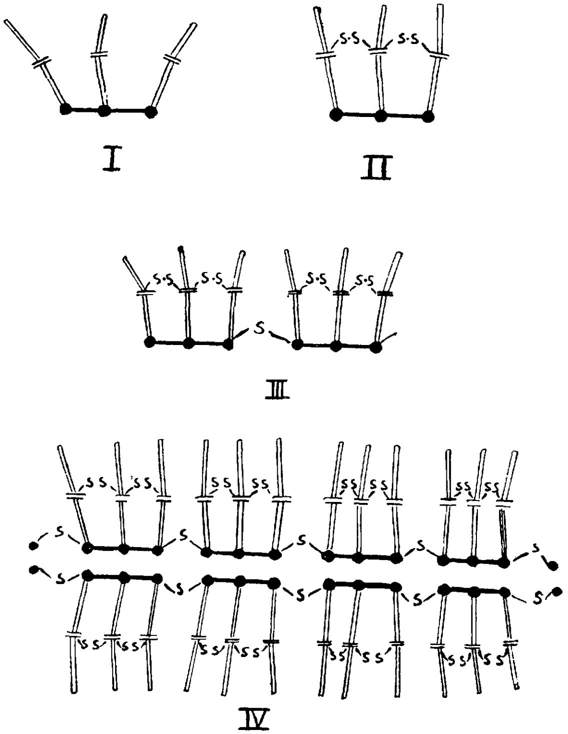
The effect of lowering the temperature is interesting (see Fig. 3). A change from 16° to 1° has very little effect on the area of the oleic acid film, but this may be subjected to a somewhat higher pressure at the lower temperature before collapsing. The oleic acid film at 0° is still considerably above its temperature of transition from the expanded to condensed type of film as shown by Adam (*Proc. Roy. Soc.*, 1926, *A*, **112**, 362). On the other hand, an equal lowering of temperature causes a considerable decrease in the film of the sulphurised oleic acid. It is evident that at 1° the latter film is much nearer to its transition temperature than is oleic acid : it is approaching the behaviour of the corresponding saturated fatty acid film. The sulphurised oleic acid is less compressible than oleic acid. These differences in behaviour are undoubtedly due to the fact that in the former substance the fatty-acid chains are held together by sulphur, the double bonds being partially saturated. The molecules are thus oriented more in the manner of a condensed film.

It is now possible to suggest a theory of the formation of the final insoluble, elastic substance. The double molecules of the benzene-soluble substance have been shown to be formed by the linking together, side by side in a definite orientation, of two single molecules. The more highly polymerised product containing at least 7 molecules (benzene-soluble, III, fairly elastic) is formed by the linking of further molecules in the same manner. This combination is between the glyceryl parts of the molecules. It seems probable, therefore, that in the final insoluble elastic product there would be long chains of molecules oriented with respect to one another side by side, with their hydrocarbon chains more or less parallel, combined by a repetition of this process.

This conception of the structure leading to the formation of the insoluble elastic substance is illustrated by the diagrams in Fig. 4. On this hypothesis, the slow change of the viscous fluid to an elastic solid may be explained by the slow orientation of the molecules to give long chains. The acceleration by heating and by ultra-violet irradiation is then due to the increased number of effective collisions, and therefore of opportunities for linking and orientation, under these conditions.

McBain has reached somewhat similar conclusions in the case of the formation of soap jellies from solution (Alexander, "Colloid Chemistry," p. 141); he says "The conclusion seems inevitable that the actual colloidal particles are the same in solution and in the true jelly, but that in the jelly the particles of neutral colloid are linked together probably to form innumerable ultramicroscopic filaments."

FIG. 4.



I. Triolein. *III. Benzene-soluble part* (*I and II*).
II. Acetone-soluble part. *IV. The elastic solid.*

In a later paper (*J. Amer. Chem. Soc.*, 1927, **49**, 2230), in order to explain the observed surface concentration found to be in excess of that required for a complete unimolecular film, McBain has put forward a theory of chains of oriented molecules extending downwards from the surface of solutions of non-electrolytes. He points out that the effect of finely ground fillers upon the strength and resiliency of rubber may be explained by this conception. The extensive surface of the finely ground filler has the rôle of orienting molecules in contact with it, and the chain effect extends with diminishing intensity into the surrounding rubber. Our view, that the increase of elasticity in the vulcanisation of triolein is due to a vectorial orientation of molecules, is in agreement with McBain's theory.

Recently, Sheppard and Keenan (*Nature*, 1928, **121**, 982) have given some interesting data for the spreading of cellulose esters on mercury. In order to explain the thinness of the films they suggest that a polymeric chain or sheet is formed one molecule thick. For this type of molecule the orientation is apparently with the chains parallel to the surface.

Summary.

1. The entrance of sulphur into triolein in vulcanisation does not change its orientation on water, and only very slightly alters the dimensions of the molecule. Elastic substances can be obtained from this product.

2. Measurements of thin films show that, in the polymerisation to such elastic substances, the molecules are linked side by side in a definitely oriented manner in long chains.

3. This work provides a basis for a theory of elastic formation in a solid.

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