

Witcogum — A New Chemurgic Elastomer

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The use of triglycerides in the rubber industry is as old as the industry itself. However, the present shortage of rubber and the necessity for conserving reclaimed rubber have given new impetus to efforts to use triglycerides to replace or extend rubber.

The extensive research on conversion of triglycerides to products useful with rubber, has resulted in the production of three distinctive classes of materials, which may be described as follows:

a. So-called "rubber substitutes," which are vulcanized oils produced by simple interaction between triglycerides and sulfur or sulfur chloride. These materials have been produced for many years by several manufacturers under various trade names, such as "Factice" and "Neophax."

b. Elastomers produced by conversion of triglycerides to dimer acids and esterifying the acids with polyhydroxy alcohols. These materials are the result of recent work, and are known by the names "Norepol," "Vulprene," or "Agripol."

c. Products in between class a and class b, which are obtained by polymerization and condensation of triglycerides in the presence of various resinous or non-elastic compounds. They are an attempt to arrive at the elastomer properties of the polyesters of class b, without using critical equipment or non-economic processes. These materials are known by the trade names "Kempol," "Sulprene," or "Witcogum."

Vulcanized Oils

The conversion of triglycerides into solids that can be incorporated into rubber is by no means a new development. The alchemists were aware of the interaction of oils and sulfur at elevated temperatures, and the use of resulting products in rubber became widespread in Europe during the middle of the 19th century.

Today vulcanized oils or so-called "rubber substitutes" find widespread use as regular rubber compounding ingredients which are incorporated into the rubber to obtain certain desirable properties or to extend the volume of finished products which can be obtained from a given amount of rubber. Because of the fact that all vulcanized oils will crumble or tear apart when subjected to even a slight degree of compression, stretching, or tearing action, they cannot be formed into useful products without the addition of some amount of rubber, reclaimed rubber, or other elastomer. For that reason they are not strictly "rubber substitutes" but more properly "rubber compounding ingredients" or "rubber extenders."

Although vulcanized oils cannot be used in place of rubber, their elastic characteristics enable them to be used in rubber in larger quantities than would be possible were they mere fillers or diluents. Printers' rollers contain up to 100% of vulcanized oils based on the rubber content, while spread goods may con-

tain 50% to 75% and erasers 100% to 300% on the rubber. In molded products such as mechanical goods or druggist sundries the content is seldom more than 15% to 25%.

The principal reason for using vulcanized oils in rubber is that they aid in processing operations. During the mixing of the rubber batch, whether it be done on the open mill or in an internal mixer, the vulcanized oil softens the stock and decreases the time necessary for the operation. It increases the rate of incorporation of pigments into the batch and the amount of pigment that can be used.

The softening action of vulcanized oils also aids the extrusion of the uncured rubber batch through tubing machines and the sheeting out of the batch by means of a calender. The addition of vulcanized oils cuts down the tendency for production of uneven surfaces and enables a greater volume of stock to be processed per unit of time. Another place where vulcanized oils aid in processing is in the spreading industry, where the spreading of fabric with rubber cement is facilitated by incorporation of vulcanized oils in the rubber batch before the cement is made.

Vulcanized oils are used to good advantage in sponge rubber stocks. They allow the stock to be successfully molded without becoming sticky, and contribute to the size and uniformity of the cell structure of the cured stock.

Other advantages which are obtained by the use of vulcanized oils are the production of a smooth velvet-like surface on the finished rubber article, the retarding of the appearance of sulfur bloom on an uncured calendered compound, and the improvement in aging which is obtained with certain types of products such as spread goods.

Today two large classes of vulcanized oils exist, the brown and the white. Both types are made from corn oil, rape seed, soya bean, linseed, or cotton seed oil, the first three being used to the greatest extent. White vulcanized oil is produced by the addition of sulfur monochloride to the oil in portions so as to avoid rapid temperature rise. To prevent rapid evolution of hydrochloric acid, small amounts of magnesium oxide or lime are added. Brown vulcanized oil is made by heating the oil with sulfur at temperatures above 160°C.

Polyester Type Elastomers

With the loss of the East Indian rubber supply it became necessary to seek new ways of supplanting the domestic supply of rubber, at least between the

TABLE 1

	A	B	C	D	E	F	G	H	I	J	K
Whole Tire Reclaim.....	0	10	20	30	40	50	60	70	80	90	100
Witcogum.....	100	90	80	70	60	50	40	30	20	10	0
Clay.....	30	30	30	30	30	30	30	30	30	30	30
Stearic Acid.....	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
Mercaptobenzothiazole.....	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Sulfur.....	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
Tensile Strength (lbs. per sq. in.).....	300	300	330	440	440	480	570	700	740	840	900
Elongation (%).....	110	130	140	160	160	190	200	250	260	300	320

TABLE 2

	A	B	C	D	E	F	G	H	I	J	K
GR-S (Buna S).....	0	10	20	30	40	50	60	70	80	90	100
Witcogum.....	100	90	80	70	60	50	40	30	20	10	0
Soft Carbon Black.....	30	27	24	21	18	15	12	9	6	3	0
Witeco No. 12 Channel Black.....	0	5	10	15	20	25	30	35	40	45	50
Zinc Oxide.....	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5
Witeco No. 20 Softener.....	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5
Mercaptobenzothiazole.....	0	.15	.30	.45	.60	.75	.90	1.05	1.20	1.35	1.5
Sulfur.....	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2
Tensile Strength (lbs. per sq. in.).....	300	370	550	750	1050	1350	1650	1950	2400	2500	2900
Elongation (6%).....	100	160	250	340	380	400	400	410	410	410	420

period when the major source was lost and the time that synthetic rubber would be produced in large quantities for civilian as well as military needs. So it was not surprising that many laboratories in this country were working on this project soon after Pearl Harbor.

The Northern Regional Research Laboratories of the U. S. Department of Agriculture was successful in developing an elastomer of the polyester type, which was named Norepol. The information necessary for commercial production of the material was released by the Northern Regional Research Laboratories when it became apparent that such information could be used to aid the war production program. The result was that Norepol type material has been placed on the market under names of Vulprene (1) and Agripol (2).

Of all the elastomers derived from glycerides the most promising from the standpoint of desirable properties have been these polyester types. The development of these elastomers was based on the idea that if triglycerides could be taken apart and put together again in the manner resembling the structure of rubber and similar high molecule weight polymers, a material would be formed which would be entirely different from any of the vulcanized triglycerides known up to now.

The procedure developed for the manufacture of these elastomers is to convert the triglycerides to dimer acids. These acids possessing two carboxyl groups are then capable of polyesterification with an alcohol containing two hydroxyl groups.

By such an esterification a viscous polyester is produced which when compounded and vulcanized yields a material strongly resembling rubber in appearance. The product possesses a tensile strength in its initial development of about 500 to 600 pounds per sq. in. with an elongation at break of 100 to 200%. It has good aging properties and good resistance to solvents. Although tensile strengths of 1000 to 2000 lbs. per sq. in. have been reported by using purified fatty acid fractions, such materials are not believed to be in commercial production.

Intermediate Products

The shortage of natural rubber and the success which the Northern Regional Research Laboratories had with Norepol prompted a number of laboratories to investigate products in between simple vulcanized oils and the polyester type elastomers. The result was the production of Kempol (3), Sulprene (1), and Witcogum (4).

While these materials have not been offered as true synthetic rubbers obtained from triglycerides, they have achieved some degree of success as elastomeric substitutes for reclaimed rubber.

Although the details of the methods used in manufacturing these products have not been revealed, it is believed that all three products are obtained by heat polymerization of vegetable oils in the presence of resinous materials. The basic chemistry involved in such polymerization is not fully understood. I. M. Bernstein (5) has pointed out that at high temperatures vegetable oils isomerize, and by intermolecular addition increase in molecular weight until a change of state occurs and the material changes from a viscous liquid to an infusible gel. He suggests two possible mechanisms by which gelation takes place:

- gelation is caused by association forces of various types; electrostatic attractions between polymer colloidal micelle, van Der Waals forces, and possibly hydrogen bond formation, and
- the gelation is due to specific solubility properties of the dimer, trimer, and tetramer oil polymers which are formed.

P. J. Flory (6) attributes gelation to the formation of network structures of indefinite extent. These giant structures make their appearance when the degree of branching or cross-linking of the polymer chains exceeds a critical value.

In the manufacture of these intermediate products the polymerization takes place in such a way that the cross-linking of the polymer chains can be inhibited so as to avoid gelation while permitting the molecular weight to increase. The introduction of resinous materials at the proper point in the process causes a co-polymerization and condensation with the triglyceride polymers, which contributes considerably to the toughness and abrasion resistance of the finished product.

Although the physical properties which can be obtained with these intermediate materials are not as good as the properties of the polyester type elastomers, they have achieved better commercial success due to the fact that they have been made in non-critical equipment, with non-critical raw materials, and by processes which are economically sound.

Properties and Uses of Witcogum

Witcogum is a resilient, black, spongy material which can be milled on a standard rubber mill and processed on regular extruders, calenders, and vulcanizing equipment. All the ingredients necessary for vulcanization are contained in Witcogum.

The tensile strength of Witcogum varies between 250 and 450 lbs. per sq. in. and the elongation at break between 100% and 150%. Although resistance to abrasion and cracking due to flexing is not comparable with that of rubber, it is sufficient for many products which are not under dynamic stress.

The material may be made harder by addition of reinforcing or inert fillers. All standard rubber pigments or fillers may be used with Witcogum. Channel carbon black may be used in small amounts with

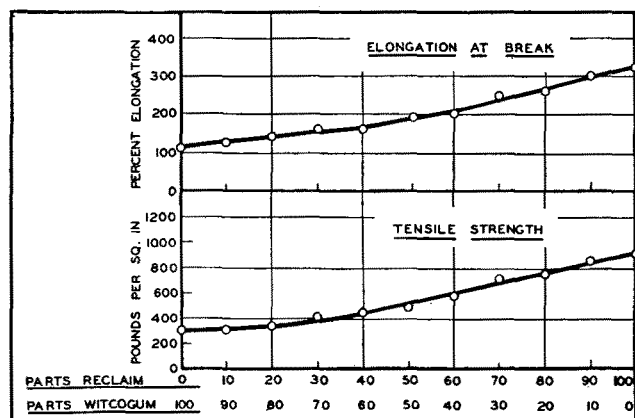


Fig. 1

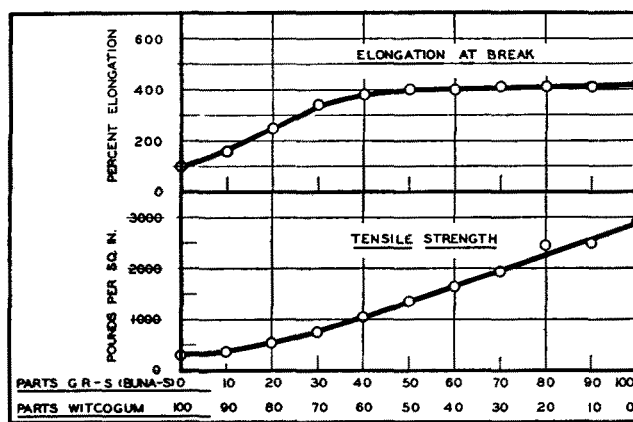


Fig. 2

other pigments, however, its use in large loadings is not recommended because of an increased tendency of the Witcogum to crack when sharply flexed. Softeners such as rosin, coumarone-indene resins, etc., may be added to Witcogum to increase tack and improve processing and molding and give a more homogeneous product.

Present information indicates that Witcogum cannot be put into solution and therefore cannot be used in cements or for proofed goods. The effect of solvents and chemicals in Witcogum is in general similar to their effect on rubber. Water and alcohol have no apparent effect but petroleum solvents, aromatic solvents, acetone and esters cause swelling with consequent loss of strength.

Although Witcogum is designed primarily for use alone, it may be blended with rubber, reclaim or synthetic rubber to improve processing or to extend these elastomers. The use of Witcogum with reclaim to improve processing is particularly interesting since it serves to soften and smooth out a batch without increasing the tackiness. The physical properties which are obtained when Witcogum is used to extend reclaim are summarized in Table 1, and in Figure 1.

Even though there is no advantage from a processing angle of using Witcogum with natural rubber there is an advantage in extending the rubber by using it. Because of the fact that it may be milled alone without any other material, large quantities of Witcogum may be used with rubber without destroying the milling qualities. Therefore, by use of Witco-

gum a small quantity of natural rubber may be made to furnish a larger volume of cured rubber compound.

With the Buna N and Buna S type synthetics the use of Witcogum serves to smooth out the sheet and improve the processing qualities in much the same way as it does with reclaim batches. Table 2, and Figure 2 show properties which result when Witcogum is used with Buna S (GR-S) type synthetic.

Witcogum is offered as a replacement for rubber and reclaim only for certain products which do not require high tensile strength, maximum elongation, or superior resistance to abrasion and flex cracking. Some of the products in which Witcogum is being used are extruded channels, jar rings, hospital sheeting, hose and tubing, wire insulation, brake linings, stationer's goods, gaskets and grommets.

The advantages of Witcogum over similar materials are that it is available in quantity and it may be milled, extruded, calendered, and cured without difficulty on standard equipment using standard rubber compounding ingredients. The present use of Witcogum by many manufacturers in the rubber industry for a wide variety of products is releasing a considerable quantity of rubber, reclaim and synthetic rubber for more essential purposes.

BIBLIOGRAPHY

1. Nazzaro, R. T., and Abramowitz, W., *Rubber Age*, 52, 483-486 (1943).
2. Braidwood, C. A., *Chemical Industries*, 52, 322-324 (1943).
3. Walton, W. T., *Rubber Age*, 53, 234 (1943).
4. Yoran, C. S., Harber, W. I., *India Rubber World*, 108, 43 (1943).
5. Bernstein, I. M., *American Ink Maker*, 21, 65-69 (1943).
6. Flory, P. J., *Journal of Physical Chemistry*, 46, 132-140 (1942).

Abstracts

Oils and Fats

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M. M. PISKUR and SARAH HICKS

A PILOT REFINING UNIT. For vegetable and fatty oil processing. D. G. Gillies. *Oil Colour Trades J.* 105, 240-3 (1944).

HIGH-VACUUM SHORT-PATH DISTILLATION — A REVIEW. K. C. D. Hickman. *Chem. Revs.* 34, 51-106 (1944).

FANWEED SEED OIL. POTENTIAL SUBSTITUTE FOR RAPESEED OIL. J. R. Clopton and H. O. Triebold. *Ind. Eng. Chem.* 36, 218-19 (1944). Fanweed (*Thalspi arvense*) seeds contain 33 to 35% oil. The compn.

and properties are similar to those of rapeseed oil. Glycerides of both oils are characterized by a high content of erucic acid. Fanweed seed oil glycerides are somewhat higher in linoleic acid than those of rapeseed oil. Viscosities of the two oils at ordinary temp. are similar, and their changes in viscosity with temp. are comparable. This property suggests that fanweed seed oil could be used in place of rapeseed oil as a lubricant constituent and for other industrial purposes.