Solvent-Resistant Rubbers Obtained by the Use of Metallic Soaps

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INTRODUCTION

Synthetic rubbers with polar groups are used when an oil- and solvent-resistant vulcanizate is sought.

The maximum oil resistance is thus obtained by using synthetic rubbers with maximum polar group content. However, this procedure brings as a consequence a decrease in the elastomeric properties of the rubber compound obtained.

A new possible way of obtaining such resistant rubbers which avoids this alternative is shown in this paper. The idea is based on the ability of some metallic soaps to thicken oils and solvents. These soaps are mixed with elastomers which are not oil-resistant. The resulting compound interacts with the solvent, forming a layer which prevents further attack. A solvent-resistant rubber can be obtained this way, without the sacrifice of its elastomeric properties.

This paper will deal with a typical oil-resistant formulation, which is also called to have flexibility at low temperature.

The customary method used to obtain these properties is given, followed by a critical comment.

The experimental part is concerned with a comparison of the behavior of formulas compounded with soap with those of similar formulas without soap.

As a conclusion, some possible uses of the new method are given.

REQUIREMENTS FOR OIL-RESISTANT RUBBER COMPOUNDS

Flexible at Low Temperature

Pure hydrocarbon rubbers, such as natural rubber SBR, and butyl rubber, are not solvent-resistant. The introduction of the CN or Cl groups in the chains gives this property.

These polar groups, with a strong interchain cohesive force, make the polymer less rubberlike.

The use of plasticizers to "neutralize" the interaction between polar groups permits the elastomer chains to have a greater freedom of motion.

A nitrile rubber, then, even with a high CN content, can be subjected to flexion at low temperature without failure. The solvent resistance of the nitrile chain remains unchanged, because the plasticizer reduces only the strength of the cohesive polar bond between the chains.

The plasticizer can be extracted or swollen by solvents. Therefore the physical properties of the vulcanizate depend upon the effect of solvent on the plasticizer, the elastomer being solvent-resistant (nitrile or chlorinated rubber).

Low viscosity plasticizers are the best for obtaining low temperature properties. Unfortunately, they are readily extracted by solvents.

One of the usual specifications, MIL-R-6855, Class I, will serve as an example of the requirements for a solvent-resistant rubber compound which is flexible at low temperature. Testing for this specification includes:

(*1*) Original physical properties of the compound.

(*2*) Change in properties after oven aging.

(*3*) Change in properties after water immersion.

(*4*) Change in properties after oil immersion.

(*5*) Change in properties after solvent immersion. This test is subdivided in three phases (*A*) immersion in aromatic solvent; (*B*) immersion in aliphatic solvent; (*C*) drying period.

(*6*) Flexibility at low temperature.

Tests for MIL-R-6855

1. Required Original Physical Properties. The tests of physical properties and values required are hardness: 40 ± 5 points, Shore A; minimum tensile strength: 1100 psi; minimum elongation: 450%. (ASTM D676-58T)

2. Oven Aging. In this test a weighed sample is placed in an oven with circulating air for 70 hr. at 100°C. The maximum allowed changes are

weight: −10%; hardness: +20 points, −0 points; tensile strength: −20%; elongation: −50%. This test includes the compression set under constant deflection, ASTM D395-55, method B (70 hr. at 100°C.). The maximum allowable difference is 40%.

Comments. A low molecular weight plasticizer has a high vapor pressure. Thus, a difference of less than 20% in weight after air aging is difficult to obtain.

Weight difference is a specific test for plasticizers. Excessive changes in tensile strength, elongation, and hardness during oven aging, however can be due to polymer overcure, polymer degradation, or plasticizer lose.

Recommended for this purpose is a plasticizer with zero volatility at 100°C., i.e., one of the polymeric type plasticizers.

3. Water Immersion Test. The sample is weighed and placed in a glass tube with distilled water for 70 hr. at 100°C. The maximum changes allowed are: hardness, ±10 points; volume, 20%, −0%.

Comments. Besides its own significance, this test gives an idea of the permanence of the plasticizers. This property is a function of the plasticizer's diffusion rate, which in turns depends on the molecular weight and the chemical structure. For this purpose, it is recommended that a plasticizer of medium to large molecular size be used. Chemically, the plasticizer must have an outstanding compatibility with the polymer.

4. Oil Immersion Test. A weighed sample is placed in ASTM oil No. 1 for 70 hr. at 100°C., in accordance with ASTM method D471-57T. The maximum changes allowed are hardness: +30 points, −0 points; volume: +10%, −30%.

Comments. An excessive change in hardness can be due to plasticizer extraction, oil incorporation, polymer overcure, or polymer degradation. Polymer overcure and degradation happen only if the curing system is not balanced. An undercured vulcanizate is easily attacked by the oil. Plasticizer extraction occurs with a low molecular weight plasticizers, while oil incorporation may happen when a polymeric plasticizer is used.

A low molecular weight plasticizer is recommended to meet the hardness and volume change requirements.

5. Solvent Immersion. To test changes on immersion in aromatic solvent (phase *A*) a weighed sample is immersed in a mixture of isooctane and toluene (75:25) for seven days at 25°C. The

maximum permissible volume change is +30%. In the second phase (phase *B*), there is subsequent immersion in an aliphatic solvent (isooctane) for seven days at 25°C. The maximum volume change related to original dimensions is −1%. Finally (phase *C*) the sample is dried in a oven with circulating air at 70°C for 4 hr. The maximum volume change related to original dimensions is −8%.

Comments. A low molecular weight plasticizer will fail in phases *B* and *C;* an extremely high molecular weight plasticizer will fail in phase *A* because of excessive swelling. The recommended plasticizer is therefore a medium molecular weight plasticizer in as a small a quantity as possible.

6. Flexibility at Low Temperature. The sample is placed in a refrigerator at −57°C. for 5 hr. At the same temperature, it must withstand an impact, without visible cracks. ASTM method D736-54 T is used.

Comments. Only low molecular weight plasticizers are supposed to give this property to oil-resistant elastomers.

Usual Methods of Compounding

The accepted methods by which the problem is being dealt with at present will be now discussed.

There are two requirements to be fulfilled by the compound: resistance to oil and solvents and flexibility at −57°C. The first is obtained by the use of highly polar rubbers. The second one is sought by means of suitable plasticizers, that is, plasticizers fulfilling the several requirements:

(*a*) Physical requirements for a suitable plasticizer include low molecular weight and low viscosity as a brittle point below −20°C. is seldom obtained with a plasticizer with a polymeric chain or a highly branched nonpolymeric chain plasticizer.

(*b*) A chemical requirement for the plasticizer is a high aniline point. This corresponds to a low "solvent power" of the plasticizer. The aniline point is defined as the temperature in which equal volumes of the plasticizer and aniline are completely miscible. Aromatics give low aniline points. A high aniline point indicates a paraffinic structure. At low temperature and equal molecular weights, an aliphatic chain has lower viscosity than an aromatic one. Thus, the best behavior at low temperature can be expected from plasticizers with high aniline points.

It is also necessary to decrease the cohesive forces between the chains to attain freedom of motion. Since the cohesive forces are due to the polar active

centers of the chain, these forces must be attenuated by a plasticizer. To achieve this, a properly "balanced" plasticizer as regard to polar components must be used.

A high molecular weight plasticizer with zero volatility at 100°C. will have a good permanence. The aniline point of the plasticizer is another variable. The lower it is, the more the "solvating" ability of the plasticizer. Therefore, a good permanence can be expected.

High molecular weight, when connected with high aniline point, thus, will indicate the plasticizer with the best permanence.[1] The specifications for changes on oil and fuel immersion makes imperative the selection of a plasticizer with a long chain, in order to prevent plasticizer extraction by the solvent. A very long chain plasticizer will swell instead of being extracted.[2] At equal molecular weight, a plasticizer with a low aniline point will behave better in the oil immersion than another one with a higher aniline point.[3] Therefore, there is a correlation between permanence and oil immersion properties.
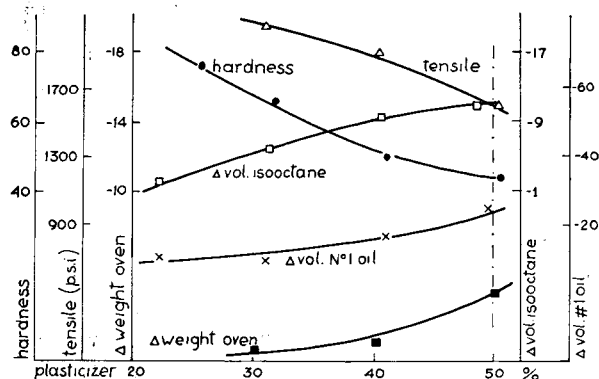

Fig. 1. Properties of rubber compound with SC plasticizer (Recipe A).
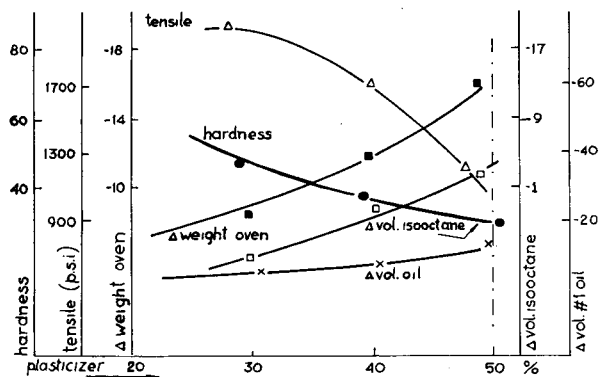

Fig. 2. Properties of rubber compound with dioctyl adipate plasticizer (Recipe A).
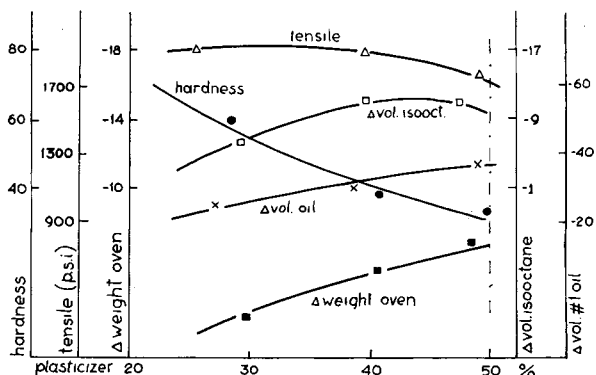

Fig. 3. Properties of rubber compound with dibutoxyethyl sebacate plasticizer (Recipe A).
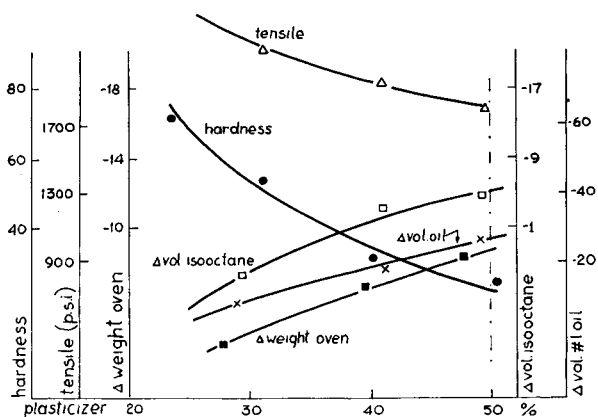

Fig. 4. Properties of rubber compound with dioctyl phthalate plasticizer (Recipe A).

Besides this particular requirement, a plasticizer must meet others which are inherent in the technical definition of plasticizers. In terms of general efficiency; the plasticizer should improve or at least not harm such physical properties as tensile strength, elongation, and resiliency. This can be better achieved with a plasticizer of medium to high aniline point.

The impairment of physical properties found after aging can be due to two factors: the migration to the surface of plasticizers of low solvent power[4] and a decrease in tensile strength and resiliency of the compound with plasticizers of high solvating power.

Water resistance is also a function of molecular size and aniline point. The best conditions are the same as for permanence and oil immersion properties. Hydrophilic groups must be avoided.

Plasticizers must be neither acid nor alkaline in order not to interfere with the cure. All these above-mentioned, opposing requirements of a plasticizer, explain why it is almost impossible to

TABLE I
Recipe A

Component	Parts
Paracril BJLT	100
Phenyl β-naphthylamine	1.4
Stearic acid	0.75
Zinc oxide	5.75
Fine thermal black	40
Precipitated silica	28
Tetraethylthiuram disulfide	1.84
Dithiodimorpholine	1.55
Benzothiazyl disulfide	1.10
Plasticizer	Variable

fulfill specifications such as MIL-R-6855 without sacrificing some properties.

Figures 1–4 show changes in physical properties of rubbers compounded according to Recipe A (Table I) with various ester-type monomeric plasticizers.

The rubbers compounded according to this recipe meet all the requirements of MIL-R-6855 but those for changes in properties on solvent immersion.

The four ester-type, monomeric plasticizers tested provide flexibility at –59°C. and meet the specifications, with the exception of the aliphatic immersion (isooctane) and the drying period (not shown in the figures).

VULCANIZATES COMPOUNDED WITH LOW MOLECULAR WEIGHT PLASTICIZERS

A plasticizer which gives flexibility at low temperature cannot withstand solvent immersion.

When a plasticized compound is immersed in a solvent, the following phenomena are possible:

(1) the solvent can be absorbed by the plasticizer;

(2) the solvent can be absorbed by the polymer;

(3) the plasticizer can pass to the solvent phase;

(4) the polymer can pass to the solvent phase;

(5) combinations of the above possibilities.

Starting with the assumption that the polymers are liquids, the plasticizer behavior can be understood in terms of behavior of a liquid–liquid mixture, which in turn is being mixed with another liquid. To complete this scheme, plasticizers can be considered solvents. Therefore, a liquid (polymer solvated by a plasticizer is in contact with another liquid (solvent).[5–9]

The miscibility of polymer and solvent, of plasticizer and solvent, and of polymer and plasticizer can be used to help predict the behavior of the plasticized vulcanizate in the solvent.

Solvation of the chain implies changes in its shape. This can be considered a plasticization of the chain, regardless of whether it is achieved by a plasticizer or a solvent.

Polar vulcanizates, such as nitrile rubber, without plasticizers, show amazing flexibility at low temperature after immersion in some solvents.[10] This plasticizing ability is greater the lower the aniline point, because this means a greater solvating power. Consequently, a greater change in the shape of the chain happens with an improvement of the flexibility.[11]

Hydrocarbon solvents, even aromatics, have very low viscosity at low temperature. This explains why an aromatic solvent behaves well at low temperature and an aromatic plasticizer does not. The main difference between plasticizers and solvents is that plasticizers decrease the binding between chains, and to accomplish this a medium to high aniline point is required.

Solvents can plasticize, but they can do it only by a different mechanism, i.e., changing the shape of the chain. This property increases the lower the aniline point. The plasticizing action of the solvent, however, is of a temporary character. The high vapor pressure of a solvent makes it a plasticizer with zero permanence. Further, a change in dimensions and in physical properties, makes undesirable this solvent action in the polymer chain.

In this ternary liquid system polymer–plasticizer–solvent, the molecular mobility of each liquid determines the kind of equilibrium attained. The polymer, being the most viscous liquid, plays the least active role. The relative mobility of plasticizer and solvent, therefore, can be considered the main factors.

A plasticizer of low mobility is swollen by the solvent, with an inherent change in shape. A plasticizer of high mobility will be easily leached out by the solvent.[11–17] In both cases it is assumed that the solvent has a great mobility. Regular solvents are used at room temperature, while oils are tested at 100°C.

None of the compounding methods presently used to obtain solvent and oil resistance take into account the possibility of reducing the molecular mobility of the solvent.

METHODS USED TO MEET REQUIREMENTS OF FLEXIBILITY AT LOW TEMPERATURE AND SOLVENT RESISTANCE

Within certain limits, it is possible to overcome the conflicting requirements of low temperature

flexibility, solvent resistance, permanence, water resistance, and oil immersion resistance, such as is the case of MIL-R-6855.

However, many theoretical requirements, such as complete solvent inertness and flexibility at below −50°C., are considered impossible to fulfill.

This implies that many technical applications in which elastomers would be used are at present considered unreachable goals.

One of the ways to obtain a compound with practically no swelling or volume decrease, is to use as much plasticizer as is possible. This plasticizer should be of a chemical composition as close as possible to that of the solvent to which it will be subjected.[4]

As the whole polymer is already solvated by the plasticizer, no change due to the solvent can be expected if plasticizer and solvent are sufficiently alike. Molecular size, polarity, aniline point, and association tendency are the variables which must be matched. However, a great quantity of plasticizer poses the danger of blooming, unless a plasticizer with low aniline point is used. This has already been done, but only at the risk of impairing the polymer's physical properties. Solvation of the polymer chains implies a sharp drop ·in the physical properties, such as tensile strength.

Another way is the use of highly extended compounds. When an inert filler is used, the relation polymer–plasticizer–solvent remains unchanged. However, all dimensional and performance changes decrease in proportion with the degree to which the compound is loaded with inert diluent. When this technique is used, some physical properties are impaired. This is shown by the fact that the specifications allow a tensile strength of 1600 psi when a hardness of 60 Shore A is required, and as low as 500 psi when Shore A hardness of 30 is specified.

Both the above-mentioned methods present used imply the use of externally incorporated plasticizers.

The method of internal plasticizing would have the advantages of the external method without its inconveniences. Although not in use today, it might be helpful to pay attention to this technique.

One method would be the use of unsaturated plasticizers, such as diallyl succinate, which can be vulcanized together with the polymer. (The work of Garvey, Alexander, Küng, and Henderson[14] deals with this subject, although not in the sense it is here dealt with.) A branched polymeric plasticizer of the above characteristics, will separate the chains due to its structure and will assure a good flexibility at low and normal temperature. How-

ever, this also implies a weak tensile strength and very low modulus.

Some highly plasticized compounds show an unexpectedly high tensile strength. This is due to a momentary sweating of the plasticizer during elongation. This explains why a plasticizer with low "solvency" gives better physical properties.

The techniques: of hyper-solvated polymer or hyper-loaded compound, which are already in use, or possibly the use of highly branched polymer can be used to obtain solvent resistance and low temperature flexibility at the price of sacrificing some other properties.

PRESENT USES OF METALLIC SOAPS

Metallic soaps are extensively used in the lubricating grease industry. In recent years, they have been used in the manufacture of plastigels.

The compatibility of elastomers and soaps has long been proved. The *Encyclopédie Générale du Caoutchouc*[26] classifies metallic soaps as plasticizers,
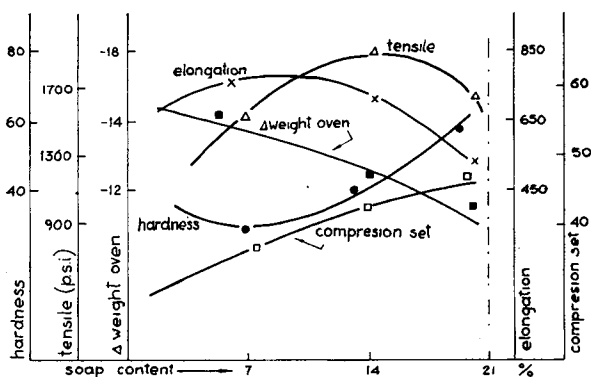

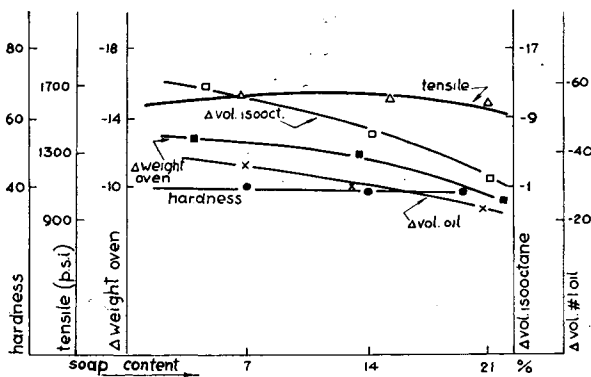Fig. 5. Properties of rubber compound containing sodium stearate (Recipe B).

Fig. 6. Properties of rubber compound containing Alumagel (Recipe B).

although their behavior is somewhat different from the average behavior of these materials. Metallic soaps are used in the rubber industry as molding aids and releasing agents.

In PVC compounding, they are used as stabilizers to prevent depolymerization due to heat and light.
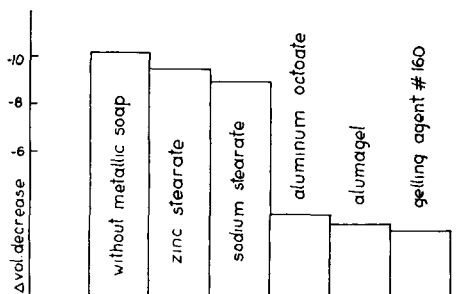

Fig. 7. Volume decrease in isooctane of hydrocarbon rubber without metallic soap and with metallic soap (5 phr).

The expected advantage of the metallic soaps in formulas for MIL-R-6855, was to reduce the volume decrease obtained after immersion in isooctane. The success in this as shown in Figures 5, 6, and 7, has led to further study.

TABLE II
Recipe B

Component	Parts
Paracril BJLT	100
Phenyl-β-naphthylamine	1.4
Stearic acid	0.75
Zinc oxide	5.75
Fine thermal black	40
Precipitated silica	28
Dithiodimorpholine	1.87
Tetraethylthiuram disulfide	1.55
Benzothiazyl disulfide	1.10
Hycar 1312[a]	13
Triethylene glycol dicaprilate	35
Metallic soap	Variable

[a] Low molecular weight liquid nitrile polymer (B. F. Goodrich Co.).

Figures 5 and 6 show the behavior of sodium stearate and Alumagel (aluminum distearate) in Recipe B (Table II) which is a slight modification of Recipe A.

Figure 7 shows a comparison among different soaps in the same Recipe B. Alumagel, Gelling Agent 160 (aluminum monostearate), and aluminum octoate (provided by Witco Chemical Co.)

readily thicken isooctane, and this explains why the compounds made up with metallic soap fulfill the solvent-resistance requirements of MIL-R-6855.

STRUCTURE AND PROPERTIES OF METALLIC SOAPS

According to experiments, metallic soaps can be considered to impart oil and solvent resistance to polymeric substances. They are susceptible to these materials, and gels obtained with them are highly viscous above their softening point. These two properties have led many authors to consider them as polymeric materials.

According to Dean,[18] they are substances more akin to rubber, polystyrene, or nitrocellulose than to compounds like aluminum sulfate. The chains of molecules are similar to linear polymers, but differ in that they can be broken up and recombined much more easily because they are not linked by the more stable C—C bonds.

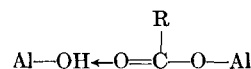The polyelectrolyte nature of the soap is also a major difference.

The polymerization or crosslinking of an aluminum soap, according to Alexander,[21] can proceed in the following way, with coordination between Al and the carbonyl:

$$\text{Al—O—}\overset{\overset{\displaystyle R}{|}}{C}\text{=O→Al—O→}$$
$$\underset{\underset{\displaystyle H}{\uparrow}}{}$$
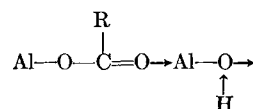
Ostwald and Riedel[19] consider that the hydrogen bonds are the means of polymerization:

$$\text{Al—}\overset{\overset{\displaystyle H}{|}}{O}\text{→HO—Al}$$

or

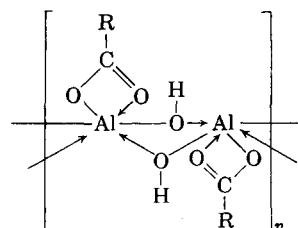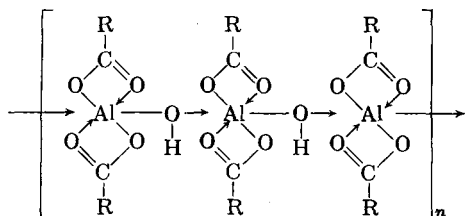$$\text{Al—OH←O=}\overset{\overset{\displaystyle R}{|}}{C}\text{—O—Al}$$
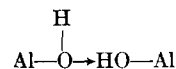
and Doscher assumes that the stability of the chains is due to the van der Waals forces.

A section of the chain of a monoaluminum soap would be assumed to have the structure:

The dialuminum soaps have structures of the type:

The chain can be desolvated by means of solvent association. Then a crystalline network will be built again, and the remaining, unattached solvent will escape. This phenomenon is known as syneresis. Doolittle[22] considers that in concentrated solutions or in weaker solvent mixtures complete solvation cannot be durably maintained. The solvent phase is always in an association–dissociation equilibrium, and the polymer is in aggregation–disaggregation equilibrium.

As soon as one point of each chain is desolvated a linear union will begin. When three or more centers are bared, a three-dimensional network is built up. This explains why in some cases crystallization can be obtained after the dispersion point.

When these chains are placed in a solvent medium and heated above their dispersion point, the soap particles are mobile and free to arrange themselves in anyway.

Coordination forces will work again when the temperature is lowered. The adjacent hydroxyl groups can be reestablished, and again, a polymer chain is formed and a network built throughout the oil.

The high viscosity demonstrated in solvents is believed to be due to crystallization forces in coexistence with the coordination bonds.

Alfrey[23] considers that portions of the macromolecular chains tend to crystallize when properly oriented. This assumption is confirmed when these soaps in solvent dispersion raise the viscosity. The rise does not continue indefinitely, for it is due to crystallization, which cannot continue since the solvation denies the opportunity of suitable orientation. A remaining portion, thus, must be bonded with polar bonds.

Addition of solvent will not change this picture,[24] even with agitation, but heat will. When melted, the former crystals are easily solvated and after cooling, crystallization is no longer possible. This is in complete agreement with practical observations, such as the coexistence of three distinct zones in a soap–solvent system.
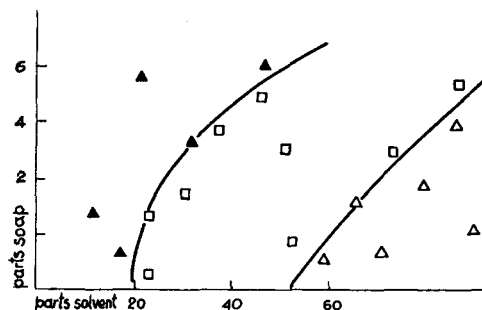

Fig. 8. Relation between soap content and physical state: (▲) swollen soap: (□) thixotropic gel; (△) nonviscous solvent.
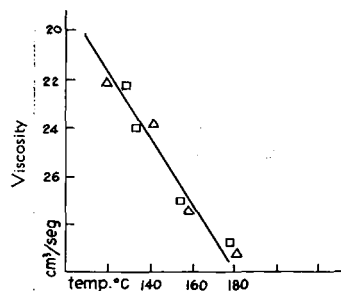

Fig. 9. Relation between (△) dispersion temperature and (□) viscosity at 20°C. ASTM oil /1 with Aluminum Octoate.

A 10-g. portion of aluminum octoate (softening point 270°C., specific gravity 103, 1% free octoic acid), was placed with 1000 g. isooctane in a closed jar and allowed to stand at 70°C. After 2 hr., three differentiated zones were visible, the upper one being constituted of mobile isooctane.

At the bottom was a constant layer of the aluminum octoate; over this there was a firm, thixotropic, transparent gel. No change occurred in the next two days. Further addition of isooctane had no effect.

The composition of each layer was determined by making several mixtures of aluminum octoate and isooctane in different proportions at constant temperature (70°F.), and stirring the mixtures. The results are shown in Figure 8.

The views of Alfrey[3] and Dean[11] are also confirmed by the following experiment. Five samples of ASTM oil No. 1, and aluminum octoate (10 g.) were mixed at 20°C. They were heated at 100, 120, 140, 160, and 180°C. respectively, until a homogeneous dispersion was formed (10°), after which they were allowed to cool at 20°C., and the viscosity was then measured (Fig. 9). The results of this experiment prove that the temperature to which the polymer is subjected will determine its

solvation rate, and this is, in turn, responsible for the viscosity.

Each polymeric soap chain has a specific dispersion temperature, which is related to the length of the chain. Separation of the chain occurs when the polar union is broken. This polar bond becomes weaker as chain length increases. Thus the dispersion temperature is inversely proportional with the chain length.

A more complex phenomenon occurs when a dispersing agent such as free fatty acid enters the system. The dispersion temperature, defined as the temperature in which the chains are separated on overcoming crystalline or polar forces decreases proportionally with increasing amount of free fatty acid.

The solvent dispersed in the soap forms the jelly phase. The thickening action of the dispersed soaps will continue until the configurational entropy equals the mixing entropy. The addition of more solvent will produce a decrease in the viscosity above this point, but this will occur only after a heating period above the dispersion point. Under the usual conditions, oil-resistant vulcanizates are required to be in contact with oil or solvents at room temperature which is usually lower than the "maximum swelling temperature" (MST). If we consider the metallic soap as a network, it will pick up solvent until the entropy of mixing is equal to the loss of configurational entropy. From experience it was found that a certain temperature (maximum swelling temperature) there is a sharp increase in the degree of solvation. At that point, the author suggests that some bonds are broken to facilitate higher solvation.

The important property of these type of gels is that at temperatures lower than MST, there will not be any solvent pickup.

Therefore, these gels will act as impermeable medium between the solvent and the rubber.

The most severe condition to which a metallic soap-compounded vulcanizate can be subjected is continuous immersion in a solvent; especially if the quantity of solvent is excessive in relation to the amount of soap and the immersion is at a temperature above the dispersion point of the soap.

At a very high temperature and with a large quantity of solvent, there is no change in performance as compared with that of a similar vulcanizate without metallic soap. However, if the proper metallic soap is selected, a higher dispersion point can be reached. In lithium stearate, for instance, there will be polar bonding up to 200°C. For practical considerations it is unnecessary to have a higher temperature range, for at this temperature thermal depolymerization begins, and destruction of the vulcanizate is produced by heat rather than the action of the oils.

A possible kinematic sequence of gel formation could be the following.[22] Metallic soap and free fatty acid are in the rubber compound; the latter must disperse the soap when in contact with the solvent. In the system formed, the specific properties of each of them will determine the amount of dissolved fatty acids, and consequently the amount of emulsified metallic soap.

The mobility of the fatty acid in the solvent determines the crystallization tendency of the soap, for it is considered that fatty acids do not permit suitable orientation of the soap molecules.

The relative mobility of the molecules of each component of the chains will be in equilibrium with that of the solvent molecules. Soap polymer[25] chains in a continuous state of reversible aggregation and aggregate breakdown will have a perpetual solvation–desolvation equilibrium, and the solvent will be engaged in an association–dissociation movement. The gel, although in continuous change in the configuration and solvation of the chains, will always have the same composition. All particles of solvent in touch with this gel will be actively engaged in maintaining the equilibrium. For every molecule of solvent which enters the network, another one leaves the soap chain, desolvating it, and enters the main body of solvent.

The number of solvatable points in these chains in the gel equilibrium range depends on the chemical characteristics of both elements. Below this equilibrium zone, another equilibrium exists. There is no sufficient number of solvent molecules to solvate the soap chains at maximum.

Another force intervenes in this stage: the tendency for crystallization of the soap. This explains why the soap chains, when desolvated, instead of building a two-dimensional polar network, will tend to orient themselves in order to find an equilibrium of a higher order. The tendency toward this stage will continue according to the fatty acid content.

Solvent molecules, in excess in the solvatable chains, will go to the equilibrium gel zone, entering it as another solvent molecule, and thus indirectly returning to the solvent mass.

The tendency toward crystallization of the soap molecules could explain why, even in continuous random solvent interchange, it is almost impossible

for solvent molecules to enter the vulcanizate mass.

The shorter the soap chain, the greater its tendency for crystallization. For this reason, in the lubricating grease industry only soaps with more than 12 carbons in the chain are used. Otherwise, in the body of the thickened oil can crystallization of the soap can begin. If this occurs, the remaining oil molecules, unable to solvate the crystallized soap, will tend to go out of this network, coming to the surface in a liquid state. This is known as syneresis.

MECHANICAL PROPERTIES OF THE SOAP CHAINS

These materials show a marked tendency for aggregation, and by means of this property, fibers are obtained. These can vary in length from 10 μ, as in sodium stearate, to 0.1 μ, as in aluminum stearate. The nature of the metal determines the fiber length; the more alkaline the metal, the longer the chain.

This will, of course, determine the physical characteristics of the gel. A shorter chain means the possibility of a closer packing; thus, a tough gel can be expected. Aluminum soaps, which have a small fiber size, give gels, which are quite impenetrable to solvent. Sodium soaps, on the other hand, are weaker in their solvent holding capacity. However, the flexural strength, as expected, favors the longer fiber. For vulcanizates which are to be subjected to flexion care must be taken in regard to this point. The flexural strength is in direct relation to the ratio of fiber length to diameter. A split means a weaker fiber. However, some fibers split lengthwise, and this will even improve their resistance.

A selection of different soaps will give the proper compound for meeting various chemical and mechanical requirements. In regard to their mixing

into the compound, the shorter the fiber, the better their dispersion. This is a very important point. As observed in experiment No. 5, sodium soaps, due to their longer fiber size, disperse poorly and have a tendency to entangle; this affects adversely several mechanical properties, such as tensile strength, elongation, and resiliency. Shorter fibers, such as those of the aluminum soaps, have no appreciable effect on physical properties, even at concentration above 20% in relation to rubber.

Figure 10 shows the behavior of the compound containing octoate at different proportions in Recipe C (Table III).

TABLE III
Recipe C

Component	Parts
Paracril BJLT	100
Phenyl-β-naphthylamine	1.4
Stearic acid	0.75
Zinc Oxide	5.75
Fine Thermal Carbon Black	77
Fine Extrusion Furnace	77
Tetra Ethyl Thiuram Disulfide	1.85
Benzothiazyl Disulfide	1.10
Dithiodimorpholine	1.57
Hycar 1312	7
Triethylene glycol dicaprilate	18
Metallic soap	As shown

It can be concluded that a ratio of 6 parts aluminum octoate to 100 parts hydrocarbon rubber is the best proportion because at greater quantities some aliphatic solvent remains in the vulcanizate. This is not in contradiction with the predictable properties of the metallic soaps, for this formulation cannot be considered complete. The use of soap in lubricating grease formulations is always accompanied by many other compounding ingredients which improve their action. None of these were used here.

CONCLUSIONS

A new method for improving resistance of vulcanizates to undesirable agents has been developed which involves the use of some polymerlike materials. The metallic soaps used are easily dispersed, and their chains quickly separate due to the weak bonding; thus they rapidly form a network within the solvent mass. In this stage they behave like other polymers, but their tendency toward crystallization prevents the possibility of solvent penetration into the polymer.

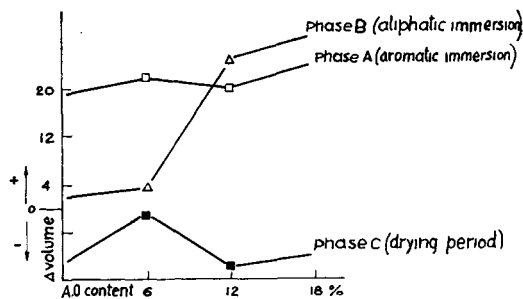No chemical change in the rubber or plastic is

Fig. 10. Change in volume of aluminum octoate-compounded recipe on solvent immersion.

TABLE IV
Comparison of Behavior of Compounds With and Without Soap

Treatment	Property	Specifications MIL-R-6855	Recipe B (without soap)	Recipe C (with soap)
Original rubber	Hardness	40	40	42
	Tensile	1100	1440	1850
	Elongation	450	725	700
Oven aging (70 hr., 100°C.)	Compression set	40%	25%	15%
	Hardness	+20 −0	+6	+8
	Tensile	−20%	+14.6%	+10%
	Elongation	−50%	−0%	−16%
Water immersion (70 hr., 100°C.)	Hardness	±10	−6	+4
	Volume	+20% −0	+4%	+1.2%
Oil immersion (70 hr., 100°C.)	Hardness	+30 −0	+16	+10
	Tensile	—	+7.5%	—
	Volume	+10 −30%	−10%	−6%
Solvent immersion				
Phase A (aromatic solvent, 7 days, 25°C.)	Volume	+30%	+9.9%	+22%
Phase B (aliphatic solvent, 7 days, 25°C.)	Volume	−1%	−9.8%	+3.6%
Phase C (drying, 4 hr., 70°C.)	Volume	−8%	−16%	−0.7%

thus necessary to give solvent resistance, with the consequent improvement in the mechanical performance.

Plasticizers with high aniline point can be used without danger of blooming.

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Synopsis

At present, solvent-resistant rubbers are obtained only by the introduction of polar groups in the polymer chain. These groups impair some physical properties of the rubber. A new way is suggested for obtaining solvent-resistant rubbers by using nonpolar elastomers compounded with metallic soaps. These soaps can be considered polymeric materials, whose long chains are built up by weak coordinate bonds, which can be easily broken and reformed in contact with solvents. In this way a layer of solvent-swollen soap is formed over the soap-compounded vulcanizate, which prevents further attack. An explanation of the above behavior is given on the basis of the crystallization tendency of the metallic soap.

Résumé

Jusqu'a présent on n'obtenait des caoutchoucs résistant aux solvants qu'en introduisant des groupements polaires dans la chaîne polymérique. Ces groupes altèrent certaines propriétés physiques du caoutchouc. On propose une nouvelle façon pour obtenir des caoutchoucs résistants aux solvants en employant des élastoméres non polaires composés de savons métalliques. Ces savons peuvent êntre considérés comme des substances polymériques, dont les longues chaînes sont formées de liens de coordination faibles qui peuvent être aisément rompues et reformées au contact des solvants. De cette manière une couche de savon gonflé de solvant se forme au-dessus du composé vulcanisé et le préserve de toute attaque ultérieure. On explique ce comportement sur la base de la tendance à la cristallisation de ce savon métallique.

Zusammenfassung

Gegenwärtig werden lösungsmittelbeständige Kautschuke nur durch die Einführung polarer Gruppen in die Polymerkette erhalten. Diese Gruppen beeinträchtigen gewisse physikalische Eigenschaften des Kautschuks. Ein neuer Weg zur Gewinnung lösungsmittelbeständiger Kautschuke durch Verwendung von unpolaren, mit Metallseifen versetzten Elastomeren wird angegeben. Diese Seifen können als polymere Stoffe betrachtet werden, deren lange Ketten durch schwache, koordinative Bindungen aufgebaut werden, die in Berührung mit Lösungsmitteln leicht gespalten und neugebildet werden können. Auf diese Weise wird über dem seifenhältigen Vulkanisat eine Schichte von lösungsmittel-gequollener Seife gebildet, die einen weiteren Angriff verhindert. Dieses Verhalten wird durch die Kristallisationstendenz der Metallseifen erklärt.

POLYMER NEWS

Society of Plastics Engineers

The Philadelphia Section of the Society of Plastics Engineers will sponsor a regional technical conference on "Polypropylene's Expanding Position in Plastics" on April 17, 1962, at the Sheraton Hotel in Philadelphia, Pennsylvania.

Roger F. Jones, research chemist with the Avisun Corporation, has been named conference chairman.