

STUDIES IN THE REVULCANIZATION  
OF RECLAIM RUBBER

by

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May 22, 1943

Prof. George W. Swett  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge, Mass.

Dear Sir:

In accordance with the requirements of the faculty, I take pleasure in submitting this thesis entitled, "Studies in the Revulcanization of Reclaim Rubber," in partial fulfillment of the requirements for the degree of Bachelor of Science.

Very truly yours,

*DA* *MA AD*  
Stanley B. Roboff *U*

### ACKNOWLEDGMENT

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SUMMARY

It is a known fact that if a ~~large~~ given quantity of rubber is vulcanized with a <sup>LARGE</sup> given quantity of sulfur in one complete batch vulcanization, the resulting product will be ebonite. On the other hand if the same vulcanization is carried out with the exception that the sulfur is added in small successive steps, the rubber being put through a reclaim process between each step, then the resulting product will not be ebonite, but rather a soft, pliable material.

It is proposed that the sulfur combines differently in the two cases. In the case of ebonite formation, it is believed that the sulfur combines intramolecularly, rendering the rubber molecule rigid. On the other hand, when sulfur is added in small steps, it is believed that it combines with the more reactive terminal unsaturated groups of the rubber hydrocarbon during the first step, there not being enough sulfur added to react intramolecularly. During the reclaim process, the rubber hydrocarbon is ruptured, giving new unsaturated end groups. Hence each time the small quantity of sulfur is added, it reacts intermolecularly with the newly formed end groups. In this way, ebonite does not form, since the sulfur never has the chance to react intramolecularly.

In order to verify the proposed theory, a means of experimental research is presented. The structure of the rubber in the two cases is to be determined by analyzing

the products of destructive distillation. Other data on the rubber hydrocarbon chain is to be determined by means of swelling and tensile strength determinations.

## INTRODUCTION

Just a bit more than a century ago, it was discovered by Goodyear that the addition of sulfur to crude rubber transformed the rubber from a weak, unflexible material to one which has far less permanent set, increased tensile strength and flexibility, and several times more resistance to heat. The term "vulcanization" is used to describe the process of sulfur addition to rubber. It is because of the process of vulcanization that rubber has achieved its present importance in society.

It has been found that rubber, after it has been manufactured into a specific product and used for considerable length of time, can be salvaged, reprocessed, and reformed into new products, just as various metals are used over again. Although reclaimed rubber does not have the exacting properties of newly vulcanized rubber, there are a great many uses to which reclaimed rubber can be put, chief among which is as a compounding ingredient with new rubber. In the year 1928 the ratio of reclaimed rubber to new rubber consumed reached a peak value of 1:2. At the present time, because of the rubber crisis, the ratio is undoubtedly far higher.

The process of reclaiming rubber has a relatively simple basis. (See Figure 1) In general, scrap rubber is passed through a "cracker" which crushes the rubber

and prepares it for grinding. It is then passed over magnets which remove loose pieces of ferrous metals. Then the rubber is fed to a shredder where it is ground into small pieces varying from one-quarter to one inch in diameter. The rubber is then blown to a cyclone separator where any pieces of loose fabric are removed. After passing over another magnet the rubber is sent to a devulcanizer or digester, where it is treated under pressure with caustic soda and steam. While in the digester, the rubber is agitated from 6 to 24 hours after which time the scrap is in a softened, more plastic state, and is swollen with water. From the digester the rubber is sent to washers, where excess caustic is removed. Then the rubber is dried, and sent to a mixing mill, where fillers, pigments, softeners, and vulcanizing agents (if necessary) are added. Finally, the rubber passes through several refining mill operations, the final product being in the form of slabs.

It has been found that in the revulcanization of reclaim rubber a strange phenomenon exists. If a given quantity of sulfur is added all at once to a given quantity of reclaimed rubber, the resulting product will be a hard rubber or ebonite. However, if the same quantity of sulfur is added to the same quantity of rubber in small successive steps, and the rubber is put through the reclaiming cycle between each step, then the final product will not be ebonite, but rather a soft,



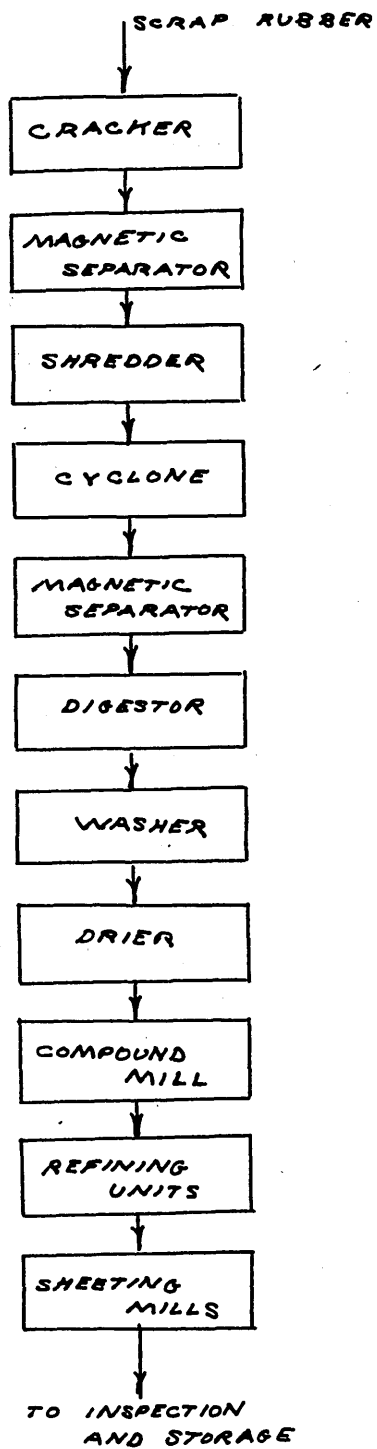
pliable rubber. This would indicate that although the same quantity of sulfur has been added to the rubber in each case, the internal structure of the rubber must be different in the two cases. It should be stressed that no sulfur is lost in the reclaim process, and that therefore the quantity of sulfur contained in the rubber in each case is the same.

Although the process of vulcanization is over one hundred years old, the exact mechanism of vulcanization is still unknown. There have been a great number of theories proposed, many of which have been discarded in the light of later knowledge. Still, there are a few theories which account for most of the reactions and properties of rubber and which have not been disproved. Therefore, if the phenomenon of sulfur addition to reclaimed rubber could be explained, a step forward will have been taken in the true explanation of the mechanism of vulcanization.

It is the purpose of this investigation to study the existing theories of vulcanization, and to determine by experimental means the mechanism of revulcanization of reclaim rubber; and to explain by these means the difference in the rubber resulting from the vulcanization to the ebonite state and that resulting from the "step wise" vulcanization to a soft rubber state.

FIG. 1

ALKALI RUBBER - RECLAIM PROCESS

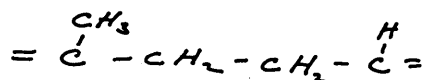


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DISCUSSION

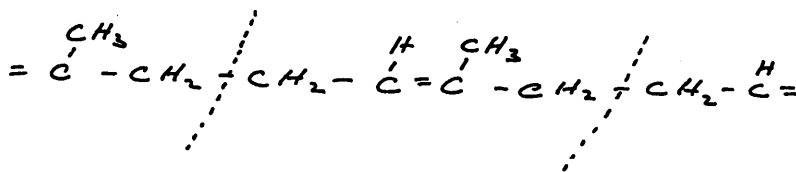
Before an investigation into the vulcanization of rubber can be made, it is necessary that a clear conception of the structure of the rubber hydrocarbon be had. If crude rubber be distilled destructively, an analysis of the decomposition products shows the presence of small quantities of isoprene and large quantities of isoprene polymers. It is also a fact that iodine or bromine will combine with rubber to give compounds whose formulas correspond to  $(C_5 H_8 X_2)_n$ , which would indicate the presence of one double bond per isoprene unit (1). Harries (2) found that after ozonolysis of the rubber, the decomposition products consisted of levulinic aldehyde ( $CH_3COCH_2 - CH_2CHO$ ), levulinic acid, and levulinic peroxide. It is known that ozone combines with an olefin at the double bond, forming an ozonide, which upon hydrolysis is decomposed <sup>to</sup> ~~of~~ an aldehyde or ketone, depending upon the position of the double bond. In addition, it is possible for the aldehyde to become oxidized to the corresponding acid. Harries therefore concluded that the nature of the decomposition products after ozonolysis clearly indicate that the general structure of the rubber molecule must contain the grouping

FIG. 2 - A



or more fully

FIG 2 B



It can be seen that the structure enclosed within the dotted lines is merely isoprene in its polymerized form.

It is clear, therefore, that all of the evidence points to the rubber hydrocarbon as consisting chiefly of isoprene units polymerized to long chain lengths. Hence, such a structure of rubber will be assumed as a basis for all further discussions in this investigation.

If an attempt is made to vulcanize rubber which has been hydrogenated with the loss of double bonds, the sulfur will not combine with the rubber, and it will be found that the ability of the rubber to become vulcanized is lost (3). This indicates that the vulcanization of rubber must include some reaction between the sulfur and the double bonds of the rubber molecule. Since it is possible to obtain two different products (ebonite or soft rubber) with the same percentage of sulfur combined with the rubber, it seems probable that sulfur reacts with rubber in more than one way. There have been several investigators who proposed that polymerization of the rubber hydrocarbon plays an important role in the vulcanization of rubber (4)(5)(6)(7). Axelrod (8) and Seidl (9) have suggested that vulcanization consists first in dipolymerization, which is followed by a polymerization under

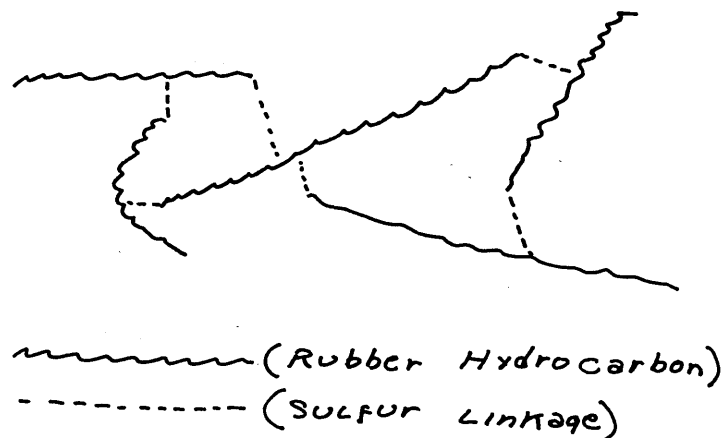
the influence of sulfur. All attempts, however, to prove that polymerization of the rubber hydrocarbons does occur have met with little or no success. Spence and Scott (10) have presented evidence based on the absorption of iodine, that there is no decrease in the unsaturation of the rubber hydrocarbon which is not directly accounted for by the percentage of combined sulfur. Changes in the specific gravity with sulfur addition also follow in linear relationships with the quantity of sulfur added, a fact which points to no polymerization during vulcanization (11)(12). It is, therefore, quite clear that during the vulcanization of rubber under ordinary means, no polymerization occurs. It is interesting to note, however, that Hauser (3)(13), and Brown (3)(13) have found that prolonged heating of rubber ~~after~~ all of the sulfur has combined results in a decrease in saturation which they attribute to polymerization of the rubber hydrocarbon. That substitution of sulfur for hydrogen during vulcanization is negligible was proved experimentally by Fisher and Schubert (14) for cases where theoretical amounts of sulfur were used.

The remaining possibility in the explanation of the mechanism of vulcanization is that the sulfur reacts with the double bonds of the rubber hydrocarbon, as has been previously mentioned. Actually, the formation of soft rubber has been accounted for by sulfur bridging between two rubber molecules (15). Further evidence presen-

ted by Boggs and Blake (16) indicates that the terminal unsaturated groups are more reactive than those in the middle of the hydrocarbon chain. Therefore in the formation of soft rubber it is likely that the sulfur combines with the terminal unsaturated groups as shown below

FIG. 3

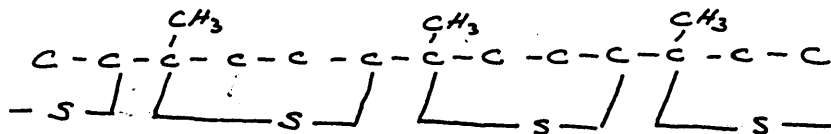
PROPOSED STRUCTURE OF SOFT RUBBER



It is most probable that the cross linking of the sulfur will involve only one terminal double bond and any other double bond which happens to be nearest. This is shown in figure 3.

The formation of soft rubber always precedes hard rubber formation, which indicates that in the formation of ebonite, intermolecular sulfur cross-bridging must first occur. Midgley, Henne, and Shepard (17) have made a proposal based on experimental evidence that in the formation of ebonite the sulfur combines with the rubber intramolecularly as shown in figure 4.

FIG 4  
PROPOSED STRUCTURE OF EBONITE



Midgley contends that perhaps the rubber molecule is extensible and is in the form of a helix, a proposal which has been offered by many investigators. If such is the case, it can be seen that the sulfur ties together successive turns of the helix rendering it rigid.

With the aid the theories so far discussed it is now possible to explain the formation of ebonite in one case and the formation of soft rubber in the other case, when reclaim rubber is vulcanized. First of all, when a given quantity of sulfur is added in one dose to a given quantity of reclaim rubber, the sulfur at first combines with the terminal unsaturated groups and then combines intramolecularly with the rubber hydrocarbon giving ebonite. In the second case, however, the sulfur is added in small successive steps, the rubber being put through the reclaim process between each step. Thus if only a small quantity of sulfur is added in the first step, then only the terminal unsaturated groups of the rubber molecule will be affected, since the unsaturation of the terminal groups must be satisfied before the sulfur

will combine intramolecularly, and since the quantity of sulfur is sufficient to fill these terminal groups only. Following the addition of the first small quantity of sulfur, the rubber is now "reclaimed". During this process, the rubber molecules are ruptured, the points of rupture not being the sulfur linkages. This means that new terminal groups have come into being, since new terminals have been created during the reclaim process. Therefore, when the second small portion of sulfur is added to the rubber, this sulfur combines just as before; that is, with the new terminal groups which have been created. The rubber is again "reclaimed", and as a result the molecules are further ruptured creating new terminal groups. Such a cycle can be continued until the same total quantity of sulfur has been added to the rubber as in the first case. In this case, however, the rubber will be soft, because each time the sulfur was added it combined intermolecularly with terminal unsaturated groups, and no intramolecular combinations, necessary for the formation of ebonite, occurred. Hence no ebonite was formed.



PROPOSED EXPERIMENTAL PROCEDURE

The experimental work in this investigation is designed to prove the explanation offered in the previous section as to why reclaim rubber can be vulcanized to two different states. This is not intended to be a description of the detailed procedure, but rather a discussion of the general method to be followed. Detailed procedures of the various methods of analysis can be found in many of the good texts on rubber (18)(19)(20).

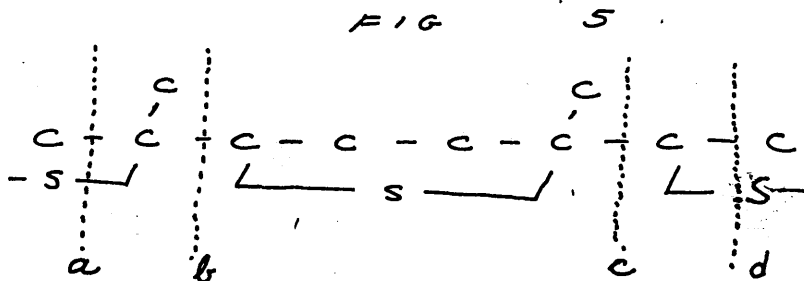
First of all a batch of unvulcanized rubber must be obtained which contains little if any impurities other than those found in natural rubber. Samples of this batch should be analyzed for sulfur in order that the absence of sulfur might be confirmed. From this batch of "pure" rubber two portions of equal weight should be removed. The first portion (henceforth known as batch A) will be used in the vulcanization to the ebonite state, while the second portion (henceforth known as batch B) will be used in the step-wise vulcanization to soft rubber. The quantity taken for each batch should be large enough so that small parts of each batch may be removed during the investigation for analysis.

It is now desirable to vulcanize both batches with 2% sulfur. The time of vulcanization should be long enough to enable all of the sulfur to combine chemically with the rubber. When the vulcanization is complete, each

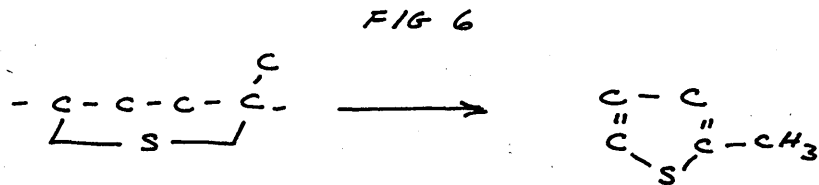
batch should be put through a reclaim process. Such a process should include grinding of the rubber, digestion under pressure with alkali and steam, washing, drying, and refining. No sulfur should be added during this preliminary reclaim. Both batches can now be considered as reclaim rubber, and therefore used as the basic constituents for the investigation.

Batch A is now ready for vulcanization to the hard rubber or ebonite state. Enough sulfur should be added to <sup>VULCANIZE</sup> the rubber to 32%. The 2% sulfur which was previously added to the rubber should be taken into account. The vulcanization should continue until most of the sulfur has combined. At this point a determination of the free sulfur should be made in order to determine the exact amount which has combined with the rubber. The rubber should now be in the form of ebonite. In order to determine the means by which the sulfur has combined, a portion of batch A should be distilled destructively, and the products of the distillation collected. By means of standard organic analysis these products can be analyzed. If the structure of ebonite is as proposed in the previous section, then the products of decomposition will consist chiefly of 2-methylthiophene; 2, 3-dimethylthiophene; 2, 4-dimethylthiophene; 2-methyl-5-ethylthiophene; and m-xylene. These products can be expected because of the rupture of the ebonite molecule during destructive distillation. It was pointed out previously that it is assumed that the

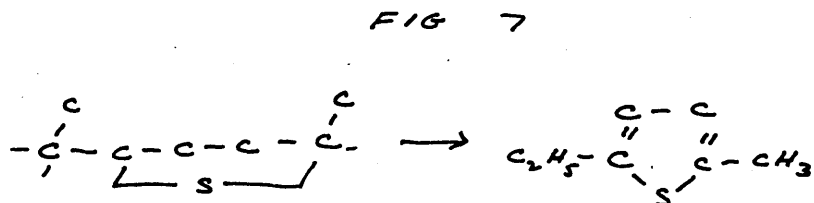
ebonite has the structure.



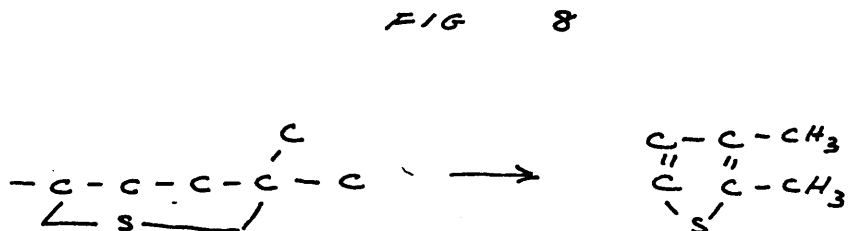
If the rupture of the molecule occurs along lines b and c 2-methylthiophene can be expected. (Fig. 6)



If the rupture occurs along the dotted lines a and c, then 2-methyl-5-ethylthiophene can be expected. (Fig. 7)

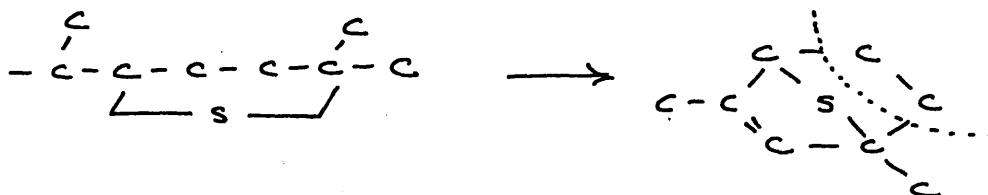


If the rupture occurs along the dotted lines b and d 2, 2-dimethylthiophene should be expected, but because of the relative unstability of such a compound, one of the methyl groups will probably migrate to the ~~beta~~<sup>beta</sup> position giving 2, 3-dimethylthiophene. (Fig. 8)



Another possibility is that the split can occur along the line a and d. In this case it is possible for the terminal carbons to link to form a six membered ring. (Fig.9)

FIG 9



The loss of hydrogen sulfide (shown by lead acetate paper) from this ring explains the formation of m-xylene, while the loss of two carbon atoms (as shown by the dotted line in figure 9) gives 2, 4-dimethylthiophene.

It is clear, therefore, that if the above compounds form the chief constituents of the products of the destructive distillation, then it is implied that the assumed structure of ebonite is probably correct.

Batch B is now ready to be vulcanized "step-wise" to the same percentage of combined rubber as was found in the ebonite. Therefore sulfur is added to batch B in 2% steps. The first 2% of sulfur should be added and the rubber vulcanized until no free sulfur exists. At this point a measurement of the degree of swelling of the rubber in carbon disulfide should be taken. Also the tensile strength of the rubber should be taken. Batch B should then be put through the reclaim process previously mentioned in this section. Following the reclaim process, the degree of swelling and the tensile strength of the rubber

should be measured. If the degree of swelling increases and if the tensile strength decreases, it can be fairly well assumed that the rubber hydrocarbon has suffered rupture during the reclaim process, giving new end groups and shorter chain lengths. This would substantiate the theory presented in the previous section. Such analyses should be conducted before and after each reclaim<sup>AND</sup> sulfur addition to rubber. When all the sulfur to be added has been added, it will be found that soft rubber exists. A portion of this rubber should now be distilled destructively, the products collected and analyzed. At the same time, a portion of the original batch of rubber containing only 2% sulfur should be subject to destructive distillation. The products of the latter distillation will probably contain isoprene, isoprene polymers, and organic sulfur compounds. The organic sulfur compounds will be present to a small degree because of the relatively small quantity of sulfur combined. Now then, if the same sulfur-organic compounds are found in the products of the destructive distillation of batch B as were found in the other case just mentioned, except that the quantity of these sulfur compounds is far greater, than it is clear that the mechanism of sulfur combination in batch B is the same as the mechanism in the 2% sulfur batch.

Since it is fairly certain in the case of rubber vulcanized with only 2% sulfur that the sulfur combines

intermolecularly, it can be safely assumed that the same mechanism of sulfur combination is present in batch B; that is, in the case of reclaimed rubber which has been vulcanized to a high sulfur content by the "step-wise" method, the sulfur combines with the rubber hydrocarbon intermolecularly.

In the above proposed procedure, it is assumed that the results of the experimental work will be positive. If such is not the case, the proposed theories will have to be modified or discarded altogether.

APPENDIX

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