Chem. Engg
Thesis

DETERMINATION OF FREE SULFUR IN RUBBER

BY

COPPER METHOD.

A Thesis submitted to the Faculty of the Massachusetts Institute of Technology as partial fulfillment of the requirements for the Degree of Bachelor of Science.

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INTRODUCTION AND SCOPE OF THESIS

The object of this thesis was to investigate further the Copper method for the determination of free Sulfur in Rubber. Briefly the method consists of extracting the free sulfur from the rubber by acetone and removing the soluble sulfur from the solution by placing copper gauze in contact with it for a period of time. The sulfur combines with the copper to form copper sulfide, and thus the increase in weight is a measure of the total free sulfur extracted.

The accepted method for the determination of free sulfur in rubber is known as the Kelly Method, and can be outlined briefly as follows:

The free sulfur in the acetone extract is oxidized by various oxidizing agents to sulfate and precipitated by Barium Chloride as Barium Sulfate, the free sulfur being calculated from the weighed Barium Sulfate.

It can be seen that this method takes considerable time and is more liable to experimental error, because of the complexity of the procedure; while the copper gauze method is very simple and requires about one-quarter of the time of the Kelly Method.

In spite of the above facts, the Kelly Method still finds favor in the Rubber Laboratories in this country. This is partly due to the following reasons:-

(1) The Copper gauze method is just at its infancy and very little information can be obtained from the literature.

(2) Very little publicity has been given to it because this method has not been standardized.

(3) There is no reliable information concerning its accuracy.

As mentioned, there is very little information and data available on this method in the literature. The main source of information is obtained from a thesis by H.A.Connor,M.I.T. '22 Course X on "The Determination of Free Sulfur in Rubber by Copper Gauze Method." In the following work the experimental details given by Mr. Connor are followed closely, and part of this work is done

on the same basis used by Mr. Connor.

COPPER GAUZE METHOD FOR THE DETERMINATION OF FREE SULFUR.

This method given below is taken from Mr. Connor's procedure on Copper Gauze Method. A few points will be raised later under "Experimental Details."

PROCEDURE:-

A sample of rubber is taken for analysis which will give about 0.03 grams of sulfur. This is extracted in soxhlet extractor overnight with acetone. A piece of copper gauze about nine square inches is cleaned by dipping it in alcohol, burning it and dipping in alcohol again while hot. This is dried to constant weight in a dessicator and weighed on a watch glass. It is put in the acetone for forty-five minutes. The copper gauze is then taken out, dipped in alcohol and allowed to stand for one hour to get rid of the resins. The copper is then dried in a dessicator to constant weight.

EXPERIMENTAL DETAILS.

(a) Copper surface required.

(1) It has been found that nine square inches of No. copper gauze can take care of as much as 0.04 to 0.045 grams of free sulfur. But it is safe to limit it to 0.03 to 0.035 grams, for the whole experiment has to be discarded if there is not enough copper put in to take care of the free sulfur.

(2) The copper has to be shining when it is put into the acetone extract or otherwise it will take a longer time than that specified in the procedure. To get the copper gauze shining, it is best to dip it into the alcohol while red hot and dry it in a dessicator.

(b) Washing and drying of Copper Sulfide.

(1) The writer has a lot of difficulties when washing the copper gauze with alcohol, for the copper sulfide very frequently falls off, so a method hasbeen devised to take care of this. The copper gauze is weighed in a 50 cc weighing bottle. When the copper is taken out of the acetone extract, it is put back into the weighing bottle, which is then filled with alcohol to wash it free of resin. After one

hour, the alcohol is decanted, for the copper sulfide is heavy enough to remain at the bottom of the bottle. The remaining alcohol can be evaporated over a steam bath and then it is dried and cooled in a dessicator.

(2) The writer doubts very much whether it pays to wash the copper gauze with alcohol. Several experiments have been run and the copper gauze is weighed before and after washing with alcohol. The following data are obtained:-

Samples used:

K_2K_7 - high resin content

K_2K_5 - low resin content

Sample	Wt. of Sample	Copper Gauze before washing	After washing	Difference	% Difference
R_2K_5	1.0324	39.0958	39.0950	.0008 gm.	0.08%
R_2K_5	.9988	37.1658	37.1650	.0008 "	0.08%
R_2K_5	1.0144	38.5252	38.5250	.0002 "	0.02%
R_2K_7	.7632	36.2076	36.2068	.0008 "	0.10%
R_2K_7	.9118	38.8864	38.8864	.0004 "	0.04%
R_2K_7	.7826	41.5674	41.5670	.0004 "	.05%

Since the sample is so taken that there will be about .03 - .04 gm. of free sulfur, then the percentage of error is about 2% to 3%. This error appears to be small when consideration is taken of the difficulty of getting a representative sample.

From the above data it can be seen that the part of the procedure which consists of washing the copper with alcohol can be dispensed with without affecting the results materially. Then the procedure can be very much simplified and much time saved.

SUGGESTED PROCEDURE.

A sample of rubber ground in a coffee copper mill is taken so that it will give about .03 - .035 gm. of free sulfur. This is best weighed in a weighing tube. The sample is extracted in a soxhlet extractor overnight or eight hours (minimum) with acetone. At the end of this time all the free sulfur should be in solution. A piece of copper gauze No. 30 mesh, about nine inches square fixed to glass handle is cleaned by heating it to red heat and dipping it in alcohol. This is

dried to constant weight in a 50 cc weighing bottle, then it is put into the acetone extract for about forty five minutes. After that it is taken out, dried and weighed in the weighing bottle. The difference in weight is the free sulfur present.

KELLY METHOD FOR DETERMINATION OF FREE SULFUR

The Kelly method was used to check the results of the copper method. Although it was accepted as the standard recently, it is by no means free from objections, which will be discussed later.

PROCEDURE.

Extract about 1 gm. of rubber overnight with acetone. Distill off the acetone on the steam bath until only 5 cc are left. The addition of several drops of ether will prevent bumping and spattering. Evaporate this at a temperature less than 60° C. When it is completely dry add 50 cc of alcohol saturated with sulfur. Heat this mixture to 50° C. for half an hour. Allow the solution to stand for four hours at room temperature. The alcohol is then poured off.

Five cc of bromine-tetra-chloride solution is added carefully. This is allowed to stand for half an hour and then 10 cc of zinc oxide-nitric acid solution is added. It is allowed to stand for about fifteen minutes and then the bromine is distilled off at a low temperature. The solution is evaporated to dryness and then the flask is heated until all the nitric oxide are driven off. The residue is dissolved in hydrochloric acid, and the solution is diluted and filtered. Barium chloride is then added to hot solution.

DESCRIPTION OF SAMPLES USED.

			Time of Vulcanization at 40# pressure.
$R_2 K_1$	Pale Crepe	100	
	Sulfur	10	4 hours
$R_2 K_2$	Pale Crepe	100	
	Sulfur	20	1 "
R_2K_3	Pale Crepe	100	
	Zinc Oxide	10	
	Sulfur	6	
	Thiocarbonilide	2	1:30
R_2K_4	Pale Crepe	100	
	Zinc Oxide	10	
	Sulfur	6	2:45
R_2K_5	Pale Crepe	100	
	Zinc Oxide	10	
	Sulfur	6	
	Dephenylguanilide	1	1:00
R_2K_6	Smoked Sheet	25	
	Soudan	75	
	Zinc Oxide	30	
	Sulfur	8	
	Thiocarbonilide	2	1:00
R_2K_7	Smoked Sheet	25	
	Soudan	75	
	Zinc Oxide	35	
	Sulfur	8	2:30
R_2K_8	Smoked Sheet	25	
	Soudan	75	
	Zinc Oxide	35	
	Sulfur	8	
	Dephenylguanidine	1	1:00

DESCRIPTION OF SAMPLES (Continued)

These samples are specially prepared by the Goodyear Tire & Rubber Company for this determination. They are so prepared that some extreme cases met in the rubber industry are taken care of.

1. Samples R_2K_6, R_2K_7 and R_2K_8 have high resin content. The purpose is to determine whether the resin has any effect on copper.
2. Samples R_2K_2 has high sulfur content.
3. Two accelerators - Thiocarbonilide and Diphenylguanidine are used.
4. Zinc oxide are used with most of the samples.
5. Carbon black is not used, as it is believed that it will not have any effect on copper.

The experimental data is divided into two parts, I and II.

Part I consists of results obtained from samples which have been previously determined by Mr. H.A.Connor.

Part II consists of results of the new sample obtained from the Goodyear Tire & Rubber Company, but the composition and time of vulcanization are identical.

ANALYTICAL DATA:-

I. (Samples from Goodyear Tire & Rubber Co. These had been previously determined by Mr. H.A.Connor, 1922).

				Average	Kelly Method			Average
R_2 K_4	4.25	4.12	4.33	4.23	3.02	2.84	2.98	2.95
R_2 K_5	2.66	2.69	2.62	2.66	1.58	1.65	1.69	1.64
R_2 K_6	4.48	4.63	4.52	4.54	4.14	4.11	4.20	4.15
R_2 K_7	4.60	4.76	4.78	4.71	No results			
R_2 K_8	3.72	3.34	3.36	3.47	"	"		

Results obtained by Mr.H.A.Connor from the above sample.

R_2K_4	Cu Method	Average	3.36
	Kelly "	"	3.33
R_2K_5	Cu Method	"	2.59
	Kelly "	"	2.55
R_2K_6	No results		
R_2K_7	Cu Method	"	4.38
	Kelly "	"	4.67
R_2K_8	Cu Method	"	4.56
	Kelly Method	"	4.92

ANALYTICAL DATA:-

II. New samples from Goodyear Tire & Rubber Co.

				Average Copper Method	Average Kelly* Method
R_2K_1	3.74	3.98	3.94	3.89	3.25
R_2K_2	16.3	16.7	16.0	16.3	13.92
R_2K_3	3.68	3.78	4.10	3.86	3.09
R_2K_4	4.01	4.26	3.97	4.08	3.25
R_2K_5	3.21	3.12	3.09	3.14	1.70
R_2K_6	No results available				4.31
R_2K_7	5.60	5.20	5.52	5.44	4.25
R_2K_8	3.72	3.94	3.58	3.75	2.67

* These results are independently obtained by the Kelly method at Goodyear Research Laboratory on identical samples.

DISCUSSION OF RESULTS.

The object in Part I is to check up the results obtained by Mr. H.A.Connor. Of the four experiments performed, only two check those of Mr. Connor's results; one is too low and the other is too high.

Sample R_2K_4 gave higher results which may be due to inexperience, for this was the first sample worked on. It is probable that Mr. Connor's results on sample R_2K_3 are too high as the Goodyear Research Division obtains lower percentage on the identical sample by the Kelly Method.

The object of Part II is to compare the results of the Kelly and Copper Methods obtained independently. The results obtained are very far apart and the Copper method shows consistently higher results than the Kelly method, but this does not show that the Copper method is at fault. In fact there are more possibilities of errors in the Kelly method.

(a) When the acetone is evaporated the flask may be overheated and some of the sulfur may be burnt off.

(b) The sulfur may be changed into inert form and becomes insoluble in carbon tetra-chloride.

(c) The alcohol which is saturated with sulfur might become supersaturated and thus carry away some sulfur when it is decanted.

(d) When Zn-HNO_3 solution is added to bromine tetra-chloride solution, there is a possibility of loss of sulfur, for a great amount of heat is generated during the oxidation of sulfur and some SO_2 or SO_3 may be driven off before it is changed to $ZnSO_4$.

(e) Precipitation and ignition of $BaSO_4$ require great care in order that pure product may be obtained.

It can be seen that the Kelly method has many possibilities of error, but the copper method is not entirely free from them either.

(a) The freshly cleansed copper may be oxidized between the time of weighing and before putting the copper in the acetone solution. This fault can be corrected by exposing the copper gauze to the air as short a time as possible and thus avoid the formation of copper oxide and sulfur. Before the copper is put into the acetone extract it should appear bright and shiny.

(b) The sulfur of the thio-compound of the organic accelerator may combine with Cu when it is soluble in acetone.

From the discussion given above, it can be seen that the Kelly method tends to give a low result and the Copper method tends to give a high one. It is believed that this is the main cause for the difference of the results obtained by the two methods. It is by no means claimed that the copper method is perfect at present but the tendency to give a higher result can be corrected and in due time it is entirely possible that it will supplant the Kelly method as a standard.

SUGGESTIONS FOR FUTURE WORK.

While the results obtained in this thesis do not indicate the method to be an entire success, still many improvements can be made. The copper gauze in this work was attached to a copper handle which was found to tarnish after the experiment. It is suggested that a glass handle be used instead of copper. This will do away with the increase in weight of the copper wire due to external sources.

It is believed that the thio-compound accelerator has a lot to do with the high results obtained with the copper method. For example, the thiocarbanild used here is partly soluble in acetone, and the sulfur of the compound, will be precipitated on the copper gauze when it is put in acetone solution. It is suggested therefore that the effect of thiocarbonild on copper be studied first, for thio-compound accelerators are very popular in the Rubber Industry at present.