

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS

SUPPLEMENT TO BUREAU CIRCULAR NO. 38

EXPLANATORY NOTE

At a conference of manufacturers and users of rubber insulation, held in New York December 7, 1911, it was decided to take steps to improve and standardize methods for analyzing rubber compounds. The interests represented at this conference were: United States Signal Corps, Bureau of Standards, American Chemical Society, New York Central Lines, Pennsylvania Railroad, General Electric Co., Hazard Manufacturing Co., Simplex Wire & Cable Co., and Standard Underground Cable Co.

In pursuance of the decision reached, a committee, now known as the Joint Rubber Insulation Committee, was appointed to devise specifications and an analytical procedure for rubber insulating compounds.

After the first report of this committee had been adopted unanimously by the conference, it was submitted to this Bureau, at the request of the committee, for tentative approval and possible publication. Because of actual participation by the Bureau in the work of the committee and because of the importance of the report on a subject in which the Bureau has long been actively interested, the report is now published as a supplement to Circular No. 38, The Testing of Mechanical Rubber Goods. It is believed that the report is a long step in the direction of standard specifications and suitable methods of analysis, the preparation of which is peculiarly germane to the work of the Bureau of Standards, and that it should prove of great value to consumer and manufacturer alike.

Its publication by the Bureau, however, must not be taken as equivalent to official indorsement by the Government or even by the Bureau itself, and the fact should not be lost sight of that the recommendations of the report are not final.

It may not be out of place to say that before this report was adopted by the conference which appointed the committee, it was submitted for criticism to chemists who were not affiliated with the conference and that it was modified in some respects to meet their views.

S. W. STRATTON,
Director.

PRELIMINARY REPORT OF THE JOINT RUBBER INSULATION COMMITTEE

[October 1, 1913.]

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PART I

GENERAL REPORT

1. At the conference of December 7, 1911, it was resolved that a committee be appointed to develop a means of specifying and analyzing rubber insulation, the committee to report its findings at a future conference.

2. The chairman of the conference, assisted by other members, appointed the following to serve upon this committee: C. R. Boggs, Simplex Wire & Cable Co.; W. S. Clark, General Electric Co.; W. A. Del Mar, New York Central & Hudson River Railroad Co.; W. B. Geiser, New York Central & Hudson River Railroad Co.; J. P. Millwood, consulting chemist; P. Poetschke, Lederle laboratories; H. B. Rodman, Pennsylvania Railroad Co.

Later, at the request of the committee, and by unanimous consent of the members of the original conference, the following were added: J. B. Tuttle, United States Bureau of Standards; E. L. Willson, Hazard Manufacturing Co.

The committee thus constituted is composed of three railroad men, three independent chemists, and three representatives of the manufacturers. Of the nine members, seven are chemists and two are engineers.

3. The committee immediately upon its formation decided to confine itself to the development of a specification and an analytical procedure for compounds of the 30 per cent Para type. In accordance with this policy it considered the available analytical procedures and developed several which formed the basis of further study. Samples of different rubber compounds were analyzed by these tentative methods. The results were unsatisfactory and the discrepancies were investigated. Subcommittees were formed to do much of this work. Twelve regular committee meetings, besides numerous subcommittee meetings, were held; 13 different compounds were distributed to be analyzed by the entire committee, and many more compounds were experimented upon by the subcommittees and individual members.

4. The outcome of this work has been a gradual elimination of errors and the development of a procedure which, with experience, will give uniform and consistent results.

5. The committee feels that the procedure which it has developed is not perfect and believes that it should be put into use for a year before being offered as final. With this in view the committee hereby presents to the conference a preliminary procedure and requests the permission of the conference to publish it and obtain the results of experience with it during the ensuing year. The committee proposes to avail itself of the experience gained in this year and to incorporate whatever improvements it may decide upon in a final report.

6. The committee has also made a study of specifications for rubber insulating compound. It presents herewith a chemical specification for a compound containing 30 per cent of Hevea rubber with mineral fillers and requests that this specification, like the analytical procedure, be considered as tentative.

7. There may still exist the possibility of making compounds which will conform to the specification when analyzed by the procedure, but which are not compounded as desired. The committee believes, however, that the probability of such compounds being supplied is very small indeed. After more experience with the procedure it may be possible to narrow the limits prescribed in the specification.

PART II

PROCEDURE FOR THE ANALYSIS OF RUBBER COMPOUND

OBJECT OF THE ANALYSIS

1. The object of this procedure of analysis is to determine whether rubber compounds comply chemically with the accompanying specification, which is intended to secure compounds containing 30 per cent of the best Hevea rubber and mineral fillers.

OUTLINE OF PROCEDURE

2. The general procedure is shown by the accompanying diagram A, which gives an outline of the separations to be effected by acetone and chloroform extractions, and saponification with alcoholic potash.

GENERAL

3. Make the analysis upon the insulation after vulcanization and, whenever possible, before the saturation of the braid. Wipe the insulation thoroughly with a damp cloth to remove any adhering material, but do not remove waxy hydrocarbons from the surface.

4. If, however, a saturated braided sample must be used, remove the braid and sandpaper the insulation to a depth of at least $\frac{5}{1000}$ of an inch and wipe with a damp cloth. In such cases report the condition of the sample.

5. Perform all determinations in duplicate and take the average value arbitrarily as the true value. Duplicate determinations must check within the limits specified.

6. Make blanks on all determinations and deduct the results accordingly.

SAMPLE

7. Remove the insulation entirely from sufficient wire to give a sample weighing about 25 grams. Cut this into small strips and grind slowly in either a No. 0 Enterprise coffee mill, or a mill such as shown by the accompanying diagram B. Adjust the grinder so that not more than 20 per cent will pass through a 40-mesh sieve. Sift all the material through a 20-mesh sieve, regrinding what is retained on the sieve until the entire sample has passed through. The wires of the sieves shall be evenly spaced in both directions and shall be of 0.016 and 0.010 inch diameter in the 20 and 40 mesh sieves, respectively. Remove with a strong magnet any metal that may have come from the grinder and thoroughly mix the sample.

EXTRACTION APPARATUS

8. The extraction apparatus shall conform with the accompanying diagram C. It shall be heated so that the period of filling an empty syphon cup with acetone and completely emptying it will be between $2\frac{1}{2}$ and $3\frac{1}{2}$ minutes.

PREPARATION OF REAGENTS

9. Acetone shall be freshly distilled over anhydrous K_2CO_3 , using the fraction 56–57° C.

10. Alcoholic KOH solution shall be of normal strength and shall be freshly made by dissolving the proper amount of KOH (purified by alcohol) in 95 per cent alcohol which has previously been distilled over KOH. The solution shall be allowed to stand for 24 hours and only the clear liquid used.

11. Ether shall be washed with three successive portions of distilled water and distilled, using the fraction 34–36° C.

12. Chloroform shall be pure and freshly distilled.

13. Carbon tetrachloride shall be pure and freshly distilled.

14. Reagents not otherwise specified shall be C. P.

ACETONE EXTRACTION

15. Extract continuously with 60 cc acetone for eight hours, two 2 g samples that have been prepared within 24 hours. Unite the extracts in a weighed flask, using hot chloroform to rinse the flasks. Distill off the reagents and dry the flask and contents for four hours at 95–100° C. Desiccate until cool and weigh. Continue to dry for 2-hour periods until constant weight is obtained. In drying place the flask on its side, but at a sufficient angle from the horizontal so that the extract does not appreciably run down the side of the flask.

UNSATURATED MATERIAL

16. Add to the acetone extract 50 cc alcoholic KOH solution, boil under a reflux condenser for two hours, and evaporate to dryness, removing all alcohol. Add 10 cc water and 20 cc ether, heat until the wax, etc., are in solution, cool, transfer to a separatory funnel, wash out the flask with warm water and, when cool, finally with two 20-cc portions of ether. The water volume should be 100 cc and the ether at least 40 cc. Shake vigorously for two minutes and allow the solutions to separate thoroughly.

Draw off the aqueous solution into a second funnel, leaving in the first funnel the ethereal solution and any flocculent material that may be present. Again rinse the flask with 20 cc ether and add it to the aqueous solution; shake vigorously for two minutes, and when separated draw off the aqueous solution and unite in the first funnel the ethereal solutions and any flocculent material. Repeat, shaking with 20-cc portions of ether until the extraction is complete, using at least 120 cc ether. Wash the flask and the funnel, from which the ethereal solution has been taken, with water, until they are free from alkali, subsequently using this wash water to wash the ethereal solution. Continue washing with water until it has been washed twice after it shows no alkaline reaction. Retain with the ethereal solution any flocculent material. Filter the ethereal solution from the flocculent material through a small pellet of extracted cotton into a weighed flask, washing first with ether and subsequently with hot chloroform, using this to rinse the original flask and both separatory funnels. Evaporate the solvents and dry the extract to constant weight at 95–100° C.; desiccate until cool and weigh.

HYDROCARBONS A

17. Add 50 cc absolute alcohol to the unsaponifiable material and warm until solution is as complete as possible. Cool the solution to -4° or -5° C, and maintain at this temperature for one hour by packing the flask in a mixture of ice and salt. Filter out the waxy hydrocarbons, using a funnel packed with ice and salt, and apply suction if necessary. Wash the flask and filter with about 25 cc of 95 per cent alcohol, which has been previously cooled to the same temperature. Catch the filtrate in a flask, which is afterwards cooled to -4° or -5° C to make sure that all possible waxy hydrocarbons have been removed, and refilter if necessary. Dissolve the residue on the filter paper with hot chloroform into the original flask. Evaporate the chloroform and dry the flask to constant weight at 95–100° C; cool in a desiccator and weigh.

HYDROCARBONS B

18. Evaporate the alcohol from the flask containing the alcohol-soluble unsaponifiable material, add 25 cc carbon tetrachloride, and transfer to a separatory funnel. Shake with conc. H_2SO_4 , drain off the discolored acid, and repeat with fresh portions of acid until there is no longer any discoloration. After drawing off all the acid, wash the carbon tetrachloride solution with repeated portions of water until all traces of acid are removed. Transfer the carbon tetrachloride solution to a weighed flask; evaporate off the solvent and dry the flask to constant weight at 95–100° C. Cool in a desiccator and weigh.

FREE SULPHUR

19. Add two grams KNO_3 to the aqueous solution and washings from the ethereal separation of the unsaponified material. Evaporate to dryness in a silver or nickel dish and heat to quiet fusion, avoiding contamination with sulphur fumes. Transfer with water to an evaporating dish, acidify

with HCl, evaporate to dryness, and dehydrate silica. Add 2 cc conc. HCl, take up in water, filter and wash, making a volume of 200 cc. Heat to boiling and add slowly a slight excess of hot 10 per cent BaCl₂ solution. Allow to stand overnight, filter, wash, ignite, weigh the BaSO₄ and calculate to sulphur.

DEFINITION OF TERMS DESCRIBING COMPONENTS OF ACETONE EXTRACT

20. The difference between the acetone extract and the free sulphur shall be called the organic extract.

21. The difference between the organic extract and the unsaponifiable material shall be called the saponifiable acetone extract.

22. The sum of the hydrocarbons A and B shall be called the total waxy hydrocarbons.

23. The difference between the unsaponifiable material and the waxy hydrocarbons shall be called unsaponifiable resins.

CHLOROFORM EXTRACTION

24. Extract continuously the residue from one of the acetone extractions (without necessarily removing the acetone that may be on it) for four hours with 60 cc chloroform, using a weighed flask. Distill off the solvent and dry the flask and contents for two hours at 95–100° C. Desiccate until cool and weigh. Continue to dry for one-hour periods until constant weight is obtained. In drying, place the flask on its side but at a sufficient angle from the horizontal, so that the extract does not appreciably run down the side of the flask. (If it is needful to wait after the acetone extraction before starting the chloroform extraction, the sample must be kept in a vacuum of at least 50 mm of mercury.)

ALCOHOLIC POTASH EXTRACTION

25. Dry the residue from the chloroform extraction at 50–60° C, put into a 200-cc Erlenmeyer flask with 50 cc alcoholic KOH solution and boil for four hours under a reflux condenser. Filter the solution into a beaker and wash twice, using each time 25 cc hot absolute alcohol, and then wash thoroughly with hot water. Evaporate the solution to approximate dryness, take up in warm water and transfer to a separatory funnel. Acidify with 15 cc 5 normal HCl, using this to rinse the beaker. Add sufficient water to make the bulk of the solution 100 cc. When cool add 40 cc ether, using it to rinse the beaker in 20-cc portions. Shake the aqueous and ethereal solutions thoroughly. After complete separation, draw off the aqueous solution and treat in another separatory funnel, with a fresh 20-cc portion of ether. Continue to shake the aqueous solution with fresh portions of ether until a colorless portion has been obtained, then shake out twice more. Unite the ethereal solutions and wash with successive additions of water, continuing twice after the water shows no acid reaction. Filter through a plug of extracted cotton into a tared flask, wash the filter and funnel with ether, evaporate the ether without boiling, and dry the residue to constant weight at 95–100° C. Cool in a desiccator and weigh.

FILLERS

26. Extract a 1-g sample with acetone for 5 hours. Transfer the residue to a tall-lipped, 200-cc beaker, add 40 cc terebene and 20 cc xylol and heat on an oil bath at 105–110° C for about 20 hours, or until the bulk of the fillers settle promptly after stirring. Occasional stirring will aid the solution. Allow the beaker to stand until the fillers and undissolved residue have settled thoroughly and decant the supernatant solution into a beaker. Add to the undisturbed residue 30 cc terebene; heat for several hours, allow to settle, decant, unite the decanted solutions and repeat this treatment as long as there is any indication of rubber being present. Continue to heat the decanted solutions during the further treatment of the undissolved residue and filter them through a tared filter paper. This filter paper must be of close texture and shall have been washed with terebene, alcohol, and acetone. The tare filter shall be treated with the same solvents and dried in the same manner throughout the analysis as the filter containing the residue. Weigh all filter papers in weighing bottles of sufficient size to take them without folding. Refilter if mineral matter runs through. Wash the beaker that contained the decanted solutions and the filter paper with benzol, using a second beaker to catch the filtrate. Add benzol to the beaker containing the residue, heat, and after settling, decant, repeating this treatment with benzol until it is thoroughly washed. Filter and wash well with benzol. Wash in the same manner both beakers with hot alcohol and then transfer the residues to the filter paper, using hot alcohol and an acetone-extracted policeman. Wash finally with acetone. Dry in air at 95–100° C and weigh. Again wash the filter paper and contents with benzol and alcohol; dry, weigh, and repeat this treatment until constant weight is obtained. Evaporate all the filtrates and washings, transfer to a porcelain dish, burn off, and weigh. Add this amount to the fillers found above. If this ash is greater than 1 per cent, the entire determination shall be repeated. Subtract 0.5 per cent as an arbitrary value for the amount of organic matter from the rubber retained with the fillers.

SULPHUR IN FILLERS

27. Transfer the fillers from the filter paper into an iron crucible; burn the filter paper and add the ash to the crucible. Add the total sulphur flux and proceed with the determination of sulphur, as in section 28, total sulphur. Subtract the percentage of sulphur found from the percentage of fillers to determine the percentage of fillers free from sulphur.

TOTAL SULPHUR

28. Mix a 0.5-g sample with 4 g Na_2O_2 and 6 g K_2CO_3 in a dry 15-cc iron crucible. Cover and heat gradually until the mixture fuses, proceeding cautiously, as rapid heating will cause an explosion, and then bring to quiet fusion for 15 to 20 minutes. Apply the heat so as to avoid contamination with sulphur fumes. Rotate the crucible while the melt solidifies. When cool, put crucible and cover into a casserole containing 200 cc of water; add 5–10 cc bromine water and boil until the melt is dissolved. Allow the

precipitate to settle, decant the liquid through a thick filter, and wash the residue with hot water. Acidify the filtrate with HCl, evaporate to dryness and dehydrate silica; add 2 cc conc. HCl, take up in water, filter, and wash, making the total volume about 400 cc. Heat to boiling and add slowly a slight excess of hot 10 per cent BaCl₂ solution. Allow to stand over night, filter, wash, ignite, weigh the BaSO₄ and calculate to sulphur.

SPECIFIC GRAVITY

29. The specific gravity shall be the ratio of the weight of a given volume of the rubber to the weight of an equal volume of water, both at 20° C. Cut strips of the largest applicable size from the conductor and use about 5 g for the sample. Determine the specific gravity in the usual manner by means of a specific gravity bottle. Care must be taken that no air bubbles adhere to the sample.

CHECKS

30. Specific-gravity determinations shall check within 0.01. The other duplicate determinations shall check within the following limits expressed as percentages of the original sample.

Determination:	Check
Acetone extract.....	0.10
Saponifiable acetone extract.....	.10
Unsaponifiable resins.....	.10
Waxy hydrocarbons.....	.10
Free sulphur.....	.05
Chloroform extract.....	.10
Alcoholic potash extract.....	.10
Fillers, free from sulphur.....	.50
Total sulphur.....	.10

INTERPRETATION

31. The rubber shall be considered to be the difference between 100 and the sum of the waxy hydrocarbons, total sulphur, and the fillers (free from sulphur), expressed as percentages. If the chloroform extract is over 3 per cent of the rubber so calculated, subtract the excess from the rubber. If the KOH extract is over 1.8 per cent of the rubber as first calculated, subtract this excess also from the rubber.

CARBON AND RED LEAD

32. Heat about 1 g of the sample with 30 cc conc. HNO₃ and 15 cc water. A black insoluble residue indicates the presence of carbon. When the rubber is dissolved in the fillers determination, the absence of any red particles indicates the absence of red lead. If red particles are present, dissolve another sample by the same method as the fillers (section 26), filter the solution through a Gooch crucible and wash thoroughly. Remove the felt and residue to a distilling flask, add HCl, and distill over the chlorine liberated by the lead peroxide, absorbing the gas in a solution of KI and starch. Not more than 0.1 cc $\frac{N}{10}$ thiosulphate shall be required to titrate the iodine liberated.

STATEMENT OF RESULTS

33. The results of the analysis shall be stated in the following form:

	Per cent
Acetone extract.....	
Saponifiable acetone extract.....	
Unsaponifiable resins.....	
Waxy hydrocarbons.....	
Free sulphur.....	
Chloroform extract.....	
Alcoholic potash extract.....	
Fillers free from sulphur.....	
Total sulphur.....	
Rubber.....	
Color of acetone extract (60 cc vol.).....	
Fluorescence in acetone extract solution (present or absent).....	
Hydrocarbons A (consistency and color).....	
Hydrocarbons B (solid or liquid).....	
Color of chloroform extract (60 cc vol.).....	
Carbon (present or absent).....	
Red lead (present or absent).....	
Specific gravity.....	

PART III

EXPLANATION OF PROCEDURE

GENERAL

1. The committee felt the more acceptable solution of its problem of drawing up a procedure which would give the percentage of rubber present in a compound with a reasonable degree of accuracy, to be the perfection and amplification of the difference method rather than the development of a direct method, which, if equally correct, might not inspire confidence because of the comparative novelty of its application to this purpose.

2. The most feasible means of limiting the kind of rubber was considered to be the determination of the saponifiable and unsaponifiable resins. These are fairly constant characteristics of the resins of Hevea rubber, and of compounds made from the same. Other methods, such as the determination of the saponification number and the optical activity of the resins, were thought to be unpractical.

3. The method as developed is applicable to the analysis of any pure rubber compound containing only mineral matter with or without ceresine or paraffine wax, regardless of the kind or amount of rubber, and can be used in conjunction with other specifications provided the limits are changed to correspond with the amount and kind of rubber desired, and due consideration is given to interfering mineral matter. When applied to a compound without ceresine or paraffine wax the unsaponifiable acetone extract is the unsaponifiable resins.

4. The method has been definitely described, to make it certain that experienced chemists may obtain concordant results. The interpretation has been rigidly defined, obviating any ambiguity as to the meaning that will be assumed, even though this sometimes appears to be arbitrary.

SAMPLE

5. In order to obtain uniform results the committee has established by experiment that a definite method of sampling has to be adopted and that for all extractions the sample must be reduced in a prescribed manner to at least an approximately similar degree of fineness. For this reason the procedure specifies a definite type of grinder obtainable in two forms, and also specifies definite sieves.

EXTRACTION APPARATUS

6. The committee has proven that the extraction apparatus used by different chemists must be of exactly the same form and the same size. It was also proven that small samples in the apparatus give the maximum results and that the rate of extraction is dependent upon the amount of solvent and its temperature as it passes through the sample. The apparatus finally adopted combines the advantages of several forms that were studied and, together with simplicity of operation and adjustment to uniform conditions, gives practically complete extraction when used as specified. A number of other variations that might have a possible effect upon the amount of extract were tried but found to be inappreciable.

ACETONE EXTRACTION

7. The extraction is made within 24 hours of the preparation of the sample, so obviating any appreciable oxidation. Two samples are extracted and united, so that a larger amount of extract may be obtained for the subsequent separations, and the extraction apparatus kept within a convenient size. Hot chloroform is used to facilitate the complete transference of the extract. The flasks are placed on their sides when drying to hasten the emission of the solvent and thus reduce chance of volatilizing, through longer heating, some of the more volatile constituents of the extract. Drying in vacuo at room temperature does not remove all the moisture if paraffine is present and such drying with heat or at 100° C in an inert gas presents no practical advantage over the method given.

SEPARATION OF THE ACETONE EXTRACT

8. The method given was developed so that all the desired constituents could be determined on one sample.

9. Emphasis is laid on thorough extraction of the unsaponifiable material and the retention of the flocculent material with the ethereal solution. This latter material is not soluble in either ether or water, but it was proven that if such as was chloroform-soluble were included in the unsaponifiable material the subsequent determination of the hydrocarbons would be more exact. A portion of this flocculent material is insoluble in chloroform.

10. The hydrocarbons are determined in two places, making an approximate separation between the solid and the liquid ones, if both are present. The first hydrocarbons (A) are those insoluble in the solvent at a low temperature. The presence of unsaponifiable resins in the solution prevents the more complete freezing out of the hydrocarbons, but the remainder is

obtained after treatment of the resins with sulphuric acid. In this way chance of loss through the action of the acid has been largely eliminated.

11. The method for free sulphur gives all the sulphur in the acetone extract with the exception of negligible amounts which may be in the unsaponifiable material. It was proven that the results agree with determinations made directly on other acetone extracts.

12. The saponifiable and unsaponifiable resins are obtained by difference.

CHLOROFORM EXTRACTION

13. The chloroform extraction should be made at once after the acetone extraction, or the sample put in a vacuum, so as to avoid the danger of an abnormally high extract. When the extract is dried as specified, constant weight is obtained before any appreciable oxidation occurs. If bituminous substances are present, that portion which has not been extracted by the acetone will be largely soluble in chloroform and can be readily distinguished by its color. The amount of extract is also affected by the presence of uncured rubber and rubber of low degree of polymerization. A properly cured Hevea compound will always give a little extract with chloroform, which varies somewhat with the method and conditions of cure.

ALCOHOLIC POTASH EXTRACTION

14. The alcoholic potash extraction is the usual saponification process for obtaining the fatty acids of rubber substitutes. The total amount of such substitutes is not obtained, but if any appreciable amount is present, the value will exceed that of the limit allowed. When no substitutes are present, this determination always yields a small amount of extract from Hevea rubber.

FILLERS

15. Since the rubber is determined by difference, it is necessary to determine the amount of fillers. Ashing the compound gives accurate results, provided no volatile or decomposable fillers are included. This, however, can not be assumed to be the case. The determination of fillers by using solvents to dissolve the rubber has always presented a difficult problem, and it is only after a great many experiments that the committee can report a reasonably satisfactory method.

16. Many kinds and probably every class of rubber solvents were tried, with the result that some did not completely dissolve the rubber at low temperatures and ordinary atmospheric pressure; others appeared to dissolve the rubber, but formed a colloidal solution holding some of the fillers which could neither be filtered nor centrifuged clear of mineral matter, and the ones that did not present these difficulties required the consumption of much time.

17. Terebene was found to be the solvent which would most completely dissolve the rubber, and after continued heating would completely destroy the rubber in solution as such, and so break up the colloidal solution. Filtering out the mineral matter is then a comparatively simple process. The treatment with terebene must be performed in the presence of air to

break up the colloidal solution. A disadvantage of using terebene is the length of time required to obtain satisfactory solution. The speed is greatly hastened if at first xylol is used with the terebene. After decanting this solution terebene is used alone. The rapidity of the action is also hastened by increasing the temperature. That specified gives reasonable speed without serious danger of carbonizing the rubber or of losing any of the fillers by decomposition.

18. It was proven that there is organic matter derived from the rubber, which is insoluble in the solvents and remains with the fillers. Without taking this into account, the fillers will appear high, and the rubber, by difference, low. As this organic matter was proven to be largely proteid matter, and this was originally a part of the rubber, an allowance is made for it. This is the amount generally retained when the method is carried out as specified. It is possible by centrifuging to throw out of the solution a great deal more than this, and it is also possible to determine the approximate amount retained in each case, but the slight increase in accuracy does not justify the extra determination.

19. Most of the details of this procedure are self-evident, but it is probably worthy of note that the benzol solutions are filtered into a separate beaker, as otherwise the benzol is apt to precipitate, from the terebene solution, organic matter which may be mistaken for mineral matter or conceal mineral matter passing through the filter. The filtrates are ashed, since traces of mineral matter are always found in them. Emphasis must be laid upon the necessity of conducting blanks on the solvents.

SULPHUR IN FILLERS

20. The sulphur in fillers is determined in order to calculate the rubber by difference. It is carried out only on the fillers obtained on the filter paper, the sulphur in the ash from the filtrate and washings being negligible.

TOTAL SULPHUR

21. Several methods for total sulphur were tried. The method given was found to yield accurate results.

INTERPRETATION OF RESULTS

22. Emphasis is laid on the method of calculating the results. The saponifiable acetone extract and the unsaponifiable resins are considered to be parts of the rubber. The chloroform and alcoholic potash extracts, when within the limits specified, are also so considered. It has been explained that the proteid matter with the fillers has been allowed for, since it also is a part of the rubber. The fillers are calculated sulphur-free, so that the sulphur will not be subtracted twice. No allowance is made for the ash in the raw rubber, as it is considered to be negligible. This method of calculation has to be adopted if the rubber found is to agree with that originally put into the compound.

MOISTURE

23. A determination of moisture is not given, as electrical tests will detect its presence if in excess. If electrical tests are required, the error introduced by the omission of this determination is very small.

NOTE.—With a procedure of this length it is impossible to explain every detail without undue elaboration, and the committee wishes to point out that while to experienced chemists the procedure may seem overburdened by detail, yet every specified detail was found necessary in order that the conditions essential to accurate and consistent work might be reproduced by all chemists using the procedure. For this reason it is extremely important that all instructions be observed, even if their significance is not perceived by the individual chemist. It will probably be found that even with the instructions properly observed, some experience will be needed to apply the method successfully.

PART IV

SPECIFICATION FOR 30 PER CENT HEVEA RUBBER COMPOUND

1. A 30 per cent fine Para or smoked first-latex Hevea rubber compound with mineral base shall be furnished. It shall contain only the following ingredients: Rubber, sulphur, inorganic mineral matter, refined solid paraffine or ceresine.

2. It shall not contain either red lead or carbon.

3. The vulcanized compound shall conform to the following requirements when tested by the procedure which forms a part of this specification.

(a) Results to be expressed as percentages by weight of the whole sample:

	Maximum	Minimum
Rubber (see section 31, Part II).....	33	30
Waxy hydrocarbons.....	4
Free sulphur.....	0.7

(b) Results to be taken between the limits given in proportion to the percentage by weight of rubber found:

	Maximum	Minimum
Limits allowed for 30 per cent rubber compound:		
Saponifiable acetone extract.....	1.35	0.55
Unsaponifiable resins.....	0.45
Chloroform extract.....	0.90
Alcoholic potash extract.....	0.55
Total sulphur (see note 3).....	2.10
Specific gravity.....	1.75
Limits allowed for 33 per cent rubber compound:		
Saponifiable acetone extract.....	1.50	0.60
Unsaponifiable resins.....	0.50
Chloroform extract.....	1.00
Alcoholic potash extract.....	0.60
Total sulphur (see note 3).....	2.30
Specific gravity.....	1.67

4. The acetone solution shall not fluoresce.
5. The acetone extract (60 cc) shall be not darker than a light straw color.
6. Hydrocarbons shall be solid, waxy, and not darker than a light brown.
7. Chloroform extract (60 cc) shall be not darker than a straw color.
8. Failure to meet any requirement of this specification will be considered sufficient cause for rejection.

NOTE 1.—Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.

NOTE 2.—This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, insulation resistance, and dielectric strength.

NOTE 3.—The limit on total sulphur may be omitted at the option of the purchaser. (See Part V of report.)

PART V

EXPLANATION OF SPECIFICATION

1. Experience has shown that compounds which upon analysis show the characteristics of good Hevea rubber may be relied upon to be more permanent than those made of rubber of other grades. It is not affirmed by the committee that a compound which conforms with this specification is necessarily permanent or that a better compound can not be made, but it is believed that enforcement of the specification will limit the use of inferior materials, and that it will put the manufacturers more nearly upon an equality of endeavor, where they can use their experience to obtain the best results. Used in connection with the analytical procedure the specification will enable purchasers to order a good compound and to ascertain with a greater certainty than heretofore whether the material received represents the compound specified.

2. The term "Hevea" applied to rubber means rubber from the *Hevea brasiliensis* tree, whether wild or cultivated, and regardless of the locality in which it has been grown. Para rubber is Hevea rubber which has been shipped from the port of Para, Brazil, and comes in several grades. Smoked first-latex Hevea rubber is a high-grade plantation rubber, which is collected prime and consists entirely of rubber which has risen in the settling vats. It is coagulated chemically and smoked in order to give it a hard cure, which insures the greatest durability. The rubber required by this specification should be Hevea rubber of good quality, such as fine Para or smoked first-latex.

3. Carbon is excluded because it is considered, by some purchasers, to be deleterious.

4. Red lead is excluded because of the possibilities of its deleterious effects on the rubber.

5. Ozokerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresine, which is permitted, is the essential constituent of ozokerite.

6. An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

7. The hydrocarbons are limited, owing to their tendency to separate from the compound and thus possibly cause porosity.

8. The free sulphur is limited because an excessive amount may be deleterious.

9. The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high acetone saponifiable extract. The minimum limit assists in forcing the use of Hevea rubber, since it is characteristic of the acetone extract from Hevea rubber to be largely saponifiable.

10. The unsaponifiable resins are limited because a low proportion of unsaponifiable resins is characteristic of Hevea rubber. A high result might be due to the presence of reclaimed rubber.

11. The chloroform extract is limited, first to prevent the use of bituminous substances, and, second, to limit depolymerized and undercured rubber.

12. The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

13. The specific gravity is limited to reconcile the specification of ingredients by weight with the practice of purchasing material by volume.

14. Fluorescence of the acetone solution is prohibited as it indicates the presence of mineral oils.

15. The color of the acetone extract is specified to conform with the normal color of the extracts from Hevea rubber. A darker color indicates adulteration or an inferior grade of rubber.

16. The hydrocarbons are required to be solid in order to prevent the use of oils and paraffine of low melting point. The shade required is that obtained from paraffine wax or ceresine. If hydrocarbons B are liquid, this would indicate reclaimed rubber softened with mineral oil, or a poor grade of paraffine.

17. The color of the chloroform extract is specified to conform with the color of dissolved gum in minute quantities. The presence of bituminous substances would be indicated by a brown or black color.

18. It would be desirable that the sulphur of vulcanization be limited to exclude reclaimed rubber, which contains the sulphur of its previous vulcanization, but the committee has not yet developed an acceptable method for determining this quantity. It is, therefore, confronted with the choice of either placing a limit on the total sulphur or giving up the attempt to exclude shoddy by sulphur limitation. Option is therefore given to the purchaser to insert or omit the limit on total sulphur. Such insertion will

at times exclude reclaimed rubber, and the committee believes it possible to make a suitable compound with this limitation. The committee thinks that a sulphur limit positively excluding reclaimed rubber would place too great a hardship, in other ways, on the manufacturers. Where the specification is used with no total sulphur limit, the use of many kinds of, or much, reclaimed rubber, will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulphur is omitted, sulphur-bearing fillers, which possess certain advantages, may be used.

19. This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assurance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact values of the limits for these tests will depend upon the use to which the material is to be put.

