

be judged from the fact that from 5000 kilos of fresh carrots (472 kilos dry) Willstätter and Escher¹ obtained only 125 g. of carotin. This is 2.5 parts in 100,000. Chemical tests for colors not infrequently have a delicacy of one part in one billion.

That carotin is contained in animal fats and oils was abundantly shown by the work of Palmer and Eckles² in the dairy laboratory of the University of Missouri, in coöperation with the U. S. Department of Agriculture.

They showed it to be contained in butter fat and the body fat obtained from cows, and further that it was not generated by the animal, but absorbed from the feed, particularly grass. Hence, it is easy to see why June butter is so highly colored. This work is confirmed by the Department of Internal Revenue³ in that the test similar to that given by palm oil would be given by an oleomargarine containing 20 per cent of butter or by oleo oils. This has been further substantiated by the work of other chemists.

In view of all these facts it would seem to be impossible to prove the presence of palm oil by this test alone in a mixture—oleomargarine, for example—in which butter (from 5–16 per cent) and oleo oil (45–50 per cent) were present, since all three contain the same substance—carotin, to which the characteristic blue color is due.

As a result of this work it would seem that the acetic anhydride or acetic acid-sulfuric acid test for palm oil is no longer available for use in connection with oleomargarine for the following reasons:

I—Unreliability of this particular test, no two chemists agreeing upon its interpretation.

II—That the test is one for carotin rather than palm oil and may be given by butter, oleo oil or sesame oil—ingredients ordinarily found in oleomargarine.

III—As applied by the Revenue Department, it is untrustworthy, because interfering oils, as sesame, are not washed out.

This communication may be regarded as preliminary, as the subject is being further studied.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE

WET COMBUSTION IN THE NITROSITE COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER⁴

By L. G. WESSON AND E. S. KNORR

In order to make more feasible the possible use in technical laboratories of the nitrosite combustion for the direct determination of rubber in rubber goods, we have attempted the application of "combustion in the wet way" to this analytical procedure.

The "nitrosite combustion" method, as described in a previous publication,⁵ is based upon the formation of the "nitrosite" of rubber by the action of nitrogen oxide gases upon the caoutchouc of the sample. This is then separated from other substances (fillers), and

burned in a specially constructed electrically heated combustion tube. The special apparatus and technique required was a decided obstacle to the general use of this method, even should its reliability be demonstrated, and we therefore turned to "wet combustion" as an escape from this difficulty.

In the course of our experiments, acetone-extracted crude rubber was first used. The nitrosite was formed in the flask used for the combustion, and after the complete expulsion of the rubber solvent (chloroform), the combustion followed in a manner quite similar to those later described. We obtained as dependable values 96.8, 97.0, 97.6, and 97.1 per cent $C_{10}H_{16}$, average 97.1 per cent; theoretical, 97.3 per cent $C_{10}H_{16}$.

In the regular analytical procedure this simple treatment of the nitrosite is not possible since the latter must be separated from the mineral matter and other impurities by the use of some solvent after filtration from the chloroform. We first used a solvent acetone, which was added to the dry nitrosite in the combustion flask. The acetone was first evaporated off, then the flask was heated $1\frac{1}{2}$ hrs. by a boiling water bath while a current of dry air passed slowly through the flask. The value now obtained (100.7 per cent) upon combustion, indicated a retention of acetone.

A repetition of this experiment with the use of only ethyl acetate as solvent gave 96.4, 97.1, and 97.0 per cent $C_{10}H_{16}$. These figures were more promising. Moreover, the ethyl acetate on evaporation left the residual nitrosite in a more porous, and thus more favorable, condition for rapid expulsion of the organic solvent than did the acetone. Ethyl acetate was therefore adopted as the solvent in all of the analyses of vulcanized rubber.

The use of acetic ester did not, however, eliminate our troubles with retained solvent, as we found when we next turned to the analysis of compounded rubber samples, instead of the raw gum. We believe that this difficulty explains most of the erratic results we had to the end of our work. We believe that we have now found the remedy for this retention of solvent in the addition of water, containing a drop of hydrochloric acid, to the nitrosite, and subsequent evaporation of this to dryness, after all solvent has been removed in the ordinary way.

In a sample¹ compounded with 35.0 per cent Fine Para, using the method described, we found 34.7, 34.9, 34.8, and 34.2 per cent $C_{10}H_{16}$, average 34.7 per cent; theoretical, 34.4 per cent $C_{10}H_{16}$.

In a sample¹ compounded with 40.0 per cent plantation rubber, we found 38.9, 39.8, 37.9, 38.1, and 37.7 per cent $C_{10}H_{16}$, average 38.5 per cent; theoretical value, 38.3 per cent $C_{10}H_{16}$.

PROCEDURE

PREPARATION OF THE NITROSITE FOR THE COMBUSTION—After the rubber sample has been ground in a meat chopper to pass a 20 mesh sieve, and $\frac{1}{2}$ g. of it extracted 3 hrs. with acetone and $\frac{1}{2}$ hr. or longer with chloroform, the extracted sample is allowed

¹ Willstätter and Stoll, "Untersuchungen über Chlorophyll," p. 241.

² *J. Biol. Chem.*, **17** (1914), 190–249

³ Evidence in court. 1915.

⁴ This article represents thesis work done by E. S. Knorr in the course for the degree of Bachelor of Science in Chemistry from the Case School of Applied Science. Read at the 53rd Meeting of the American Chemical Society, New York City, September 25–30, 1916.

⁵ L. G. Wesson, *THIS JOURNAL*, **6** (1914), 459.

¹ These samples were kindly sent us by the Bureau of Standards

to dissolve in, or thoroughly absorb, chloroform. A small Florence flask (75 cc.) is used, which may be about one-half full of the solvent. Nitrous oxide vapors, evolved from dilute nitric acid (sp. gr. 1.3) and arsenic trioxide, are then passed through the cooled chloroform until the deep green color becomes permanent for about 15 min., and the whole allowed to stand over night for completion of the action.

The chloroform is then decanted through a dry Gooch crucible and asbestos mat (the former rests in an ordinary 60° filter funnel) into the combustion flask, from which the chloroform is then evaporated by means of a boiling water bath and a dry air current.¹ Meanwhile the residue in the Florence flask has been similarly dried. The separation of fillers and nitrosite is now brought about in the following way: Small portions (5 cc.) of calcium chloride-dried ethyl acetate are added to the residue in the Florence flask, the latter warmed, and the liquid decanted through the Gooch crucible into the combustion flask, repeatedly, until the filtrate runs through entirely colorless. After evaporation of the acetate (recovery of the solvent as well), the residue is carefully freed from solvent by warming the containing flask in a boiling water bath for about 15 min., after which 15 cc. of water, containing 1 drop conc. HCl, is added, and quickly evaporated by the use of a boiling calcium chloride bath and brisk current of dry air. The heating is continued at least 1½ hr. after the residue is again apparently dry.

THE COMBUSTION APPARATUS consists of a 200 cc. round-bottom distilling flask, which is provided with a dropping funnel (100 cc.) through a one-hole rubber stopper, and a series of U-tubes containing in order, (1) conc. H₂SO₄-K₂Cr₂O₇, renewed every 1 or 2 combustions, (2) water containing a drop of the preceding, (3) granular zinc, (4) calcium chloride, (5) soda-lime (weighed), (6) soda-lime and calcium chloride (weighed).

THE COMBUSTION—The weighed soda-lime tubes in position, and the combustion flask cooled by water, a volume (20 cc.) of cooled concentrated sulfuric acid is run rapidly into the flask onto the nitrosite; then the cooled oxidizing solution of 10 g. pulverized K₂Cr₂O₇ in 75 cc. conc. H₂SO₄, in a very slow stream. The flask may now be gently warmed by a sand bath to obtain a moderately rapid evolution of gas.² This is done as long as gas continues to be evolved (about an hour), when a carbon dioxide-free current of air, the heating being maintained, is passed *via* the dropping funnel through the apparatus for at least 1½ hr. to sweep all carbon dioxide into the soda-lime tubes. $\text{Wt. CO}_2 \times \frac{136}{440} \times 200$ gives percentage C₁₀H₁₆ in the sample.

We hope, in conclusion, that further study and im-

¹ Mr. J. B. Tuttle of the Bureau of Standards has found that the chloroform-soluble residue thus recovered may be very appreciable, and it is to his suggestion that this modification is due.

² That carbon monoxide is formed during the combustion can be shown by allowing the gases which have passed the absorption train to come in contact with heated copper oxide and then barium hydroxide solution. A precipitate ensues, but the amount is not appreciable for the results of the analysis.

provements of this method will eventually give a reliable and not too difficult procedure for the direct determination of rubber, not only in good quality compounds but also in factis and other inferior substitute-containing rubbers.

CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO

DETERMINATION OF MINERAL FILLERS IN RUBBER ANILINE METHOD

By OTTO H. KLEIN, JOHN H. LINK AND FRANK GOTTSCH

Received October 23, 1916

Although the use of aniline as a solvent for vulcanized rubber is not new, there is very little information to be found concerning such use in the literature. We have, therefore, thought that an account of the method as far as it has been worked out, together with some analyses of samples of known composition, would be of interest.

This report should be considered as a preliminary one, as the supply of rubber mixings at hand for our experiments was limited and other rubber fillers than those used are yet to be experimented with.

In making the determination it is essential that the sample be finely powdered (20 mesh). A 1-gram sample is extracted with acetone for 4 hours, dried at a low temperature, and then transferred to a weighed 100 cc. centrifuge tube. The residue is covered with 50 cc. of pure aniline, 5 cc. of nitrobenzene added, the mixture stirred, covered, and heated at 160° C. with occasional stirring until solution is complete.

It is our practice to heat the samples over night in a Preas oven. In most cases solution is complete by the next day. Sometimes the sample dissolves in 3 to 4 hours. If the rubber is not yet in solution, this can be seen by stirring with a glass rod. When solution is complete, there is nothing to be seen but fine pigment, free from rubbery appearance.¹ The tube is allowed to cool sufficiently, filled up with ether and well stirred. It is then centrifuged for 15 minutes at 1500 r. p. m.

The supernatant liquid is decanted, about 25 cc. of ether added and the pigment stirred up completely. It is centrifuged again and the decantate added to the first. Four such washings with ether are necessary. The tube is dried at 100° C., cooled and weighed. The united decantates are evaporated and then ignited in a weighed porcelain or silica dish; the weight of fillers found is added to that in the tube.

The percentage of fillers plus that of total acetone extract is subtracted from 100 per cent, and the difference recorded as *rubber gum*.

Aniline differs from other solvents in that rubber dissolved in it forms a thin solution which permits the mineral fillers to separate readily.

The small amount of nitrobenzene used, causes a more rapid solution. It was found that semicured compounds dissolve more slowly than thoroughly cured soft stocks or very hard ones. With under-cured compounds a soft pasty mass is formed, which

¹ The chemist who makes the analysis for the first time may be uncertain of himself at this point, but after one or two determinations have been made he will at once recognize any undissolved rubber.