The curve for surface tension is decidedly irregular but shows a tendency to slope upwards. This indicates that among petroleum hydrocarbons surface tension varies in the same direction as specific gravity. This constant is, however, so strongly affected by small variations in chemical composition that it is at present of little value as a means of identification. It is hoped, however, that later these irregularities may be understood well enough to furnish scientific as well as useful industrial information.

Capillary constant curves show the same irregularities as those of surface tension but lack the slope upward. This is to be expected when the method of derivation of this constant is considered.

In considering the "molecular-weight" graph, it appears that the agreement of this constant with

TABLE V—PHYSICAL CONSTANTS OF "NAPHTHA" AND "KEROSENE" CUTS OF OILS STUDIED

NAPHTHA—B. P. UP TO 150° C.					KEROSENE—B. P. 150° TO 300°				
Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.	Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.
815	0.706	1.392	19.96	5.82	815	0.789	1.437	24.73	6.44
764	0.716	1.398	20.54	5.88	764	0.790	1.438	25.07	6.50
816	0.722	1.400	20.02	5.69	816	0.792	1.439	23.96	6.20
1336	0.726	1.402	20.52	5.79	765	0.795	1.440	24.66	6.43
765	0.731	1.405	19.34	5.57	1336	0.808	1.445	25.59	6.49
269	0.733	1.406	21.12	5.92	1281	0.811	1.448	26.80	6.66
Heald	0.734	1.406	20.38	5.69	1339	0.814	1.449	23.91	6.02
1339	0.736	1.407	19.41	5.41	1280	0.815	1.451	25.04	6.30
1280	0.741	1.410	20.28	5.61	269	0.820	1.452	23.18	5.77
S. M.	0.744	1.410	21.34	5.87	Heald	0.824	1.454	25.27	6.28
273	0.750	1.412	20.74	5.67	R. R.	0.836	1.458	26.34	6.45
R. M.	0.765	1.418	22.37	5.99	R. M.	0.841	1.459	26.57	6.46
					273	0.842	1.463	25.50	6.20
					S. M.	0.849	1.466	26.40	6.37
					Mex.	0.861	1.475	26.96	6.40
					Kern	0.878	1.476	27.79	6.48
					591	0.878	1.476	26.87	6.26

specific gravity, though theoretically to be expected, is conspicuous by its absence. No satisfactory explanation appears except that there is some inherent error in the method here employed for the determination of molecular weights. Present experience indicates that the measurement of this constant by the cryoscopic method with benzol as a solvent is of doubtful value in the identification of petroleum distillates. The experimental values are recorded with a full knowledge of their being "so-called Molecular Weights."

CONCLUSIONS

I—The present series of experiments has tended to justify the methods of identification (distillation, specific gravity and refractive index) usually employed in petroleum testing laboratories.

II—Volatility and specific gravity are the two most important constants and a knowledge of these two is generally sufficient for the identification of an oil.

III—Refractive indices vary in the same direction as specific gravities. When only small quantities of distillates are available, determinations of the former are more convenient than measurements of specific gravities.

IV—Surface tension is a constant not yet of value. This is on account of our lack of knowledge regarding variations caused by the probable presence of small quantities of certain substances in crude petroleum. Surface tensions in general seem to increase with specific gravity when relations among petroleum hydrocarbons are considered.

V—Cryoscopic "molecular weights," as measured by the cryoscopic method with benzene as a solvent, are of questionable value in the study of mixtures of petroleum products.

The experimental work connected with the determinations reported in this paper was carried out in the laboratories of the Departments of Physical Chemistry and Industrial Chemistry of Columbia University, New York.

CHEMICAL SECTION OF PETROLEUM DIVISION
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THE SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME AND ITS DETERMINATION BY A NEW SOLUTION METHOD

By FRANK GOTTSCH

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The following methods for the chemical analysis of rubber goods are those in use at Mt. Prospect Laboratory, Department of Water Supply, Gas and Electricity, City of New York. These methods contain certain matter original with the author, under the headings of "MINERAL FILLERS," "FOREIGN ALCOHOLIC POTASH EXTRACT," "VULCANIZED RUBBER GUM BY WEIGHT," and "VULCANIZED RUBBER GUM BY VOLUME." The method for "FREE SULFUR" is novel in the application of a well-known method for total sulfur to the free sulfur determination.

METHODS OF TEST

SAMPLES—Samples shall be taken representative of the lots to be tested.

BLANKS—Blanks shall be run and deductions made according to the lots of reagents.

CHECKS—In the event of any determination not falling within the limits given in the specifications, a check test shall be made before the report is sent out.

PREPARATION OF SOFT RUBBER—Prepare a sample of not less than 25 grams, taking pieces from various parts of the original sample. The backing of fire hose shall be buffed off before grinding; in all other hose, separate samples of tube and cover shall be made, without removing the backing or friction compound. Other rubber goods built up with friction fabric shall have the rubber layers ground up without removal of the adhering rubber friction.

GRINDING—The sample shall be cut into small pieces and then run through the grinder, taking for analysis only such material as will pass a standard 20 mesh sieve. Care must be taken to see that the grinder does not become appreciably warm during the grinding. If the nature of the material is such that it gums together so that it will not pass through the sieve, as would be the case with undervulcanized samples, it will be sufficient to pass the material through the grinder twice and accept all the material for the final sample. Crude rubber shall be cut with scissors.

Pass a strong magnet through the sample to remove any metal from the grinders, mix thoroughly, and put in tightly stoppered bottles. Do not expose to sunlight or heat.

HARD RUBBER—Samples of this material shall be prepared for analysis by rasping.

REAGENTS—Acetone shall be distilled not more than 10 days before use over anhydrous potassium carbonate, using the fraction 56 to 57° C.

Alcoholic potash shall be of normal strength, made by dissolving the required amount of potassium hydroxide in absolute

alcohol the day before use, and allowing to settle. Only the clear solution shall be used.

Barium chloride solution shall be made by dissolving 100 grams of barium chloride in one liter of distilled water, and adding two or three drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated on the steam bath over night, and filtered through S. & S. 589 blue-ribbon filter paper.

Turpentine shall be redistilled.

All reagents shall be of C. P. quality.

ANALYSIS

ACETONE EXTRACT—Place a two gram sample, which has been ground not more than 24 hours before, in an acetone extracted paper thimble, and insert in a glass syphon cup (E. & A. 1913, No. 2846) under a condenser (E. & A. 1913, No. 2848). Dry and weigh, by means of a wire loop, a clean 8 in. $\times$ 1 $\frac{1}{4}$ in. test tube weighing between 20 and 40 grams, pour in 50 cc. acetone, connect the apparatus, and extract continuously for 7 hours in such a manner that the drops of condensed solvent fall directly on to the ground rubber, and the syphon cup fills between 2 $\frac{1}{2}$ and 3 $\frac{1}{2}$ minutes, that the discharge of the syphon cup does not appreciably interrupt the boiling, that the condensed solvent filters rapidly through the paper thimble, and that no fine particles of rubber or fillers are carried over. If the solution in the cup is colored after seven hours' extraction, the extraction shall be continued for four hours the next day. Evaporate off the acetone from the tube in a slanting position over live steam, wipe off the outside with a clean linen cloth, and dry to constant weight in the water oven at 95 to 100° C., or until the weight increases, cooling in a desiccator. Calculate and record as "total acetone extract."

FREE SULFUR—Entirely transfer the residue from the tube to a 60 cc. iron or nickel crucible (E. & A. 1913, No. 2366) by acetone, chloroform, or benzol, evaporate off the solvents on the steam bath and add six grams of potassium carbonate and four grams of sodium peroxide. Mix by rotating the crucible, cover, heat at a low temperature over an asbestos shield to avoid sulfur fumes, until the mixture fuses, then bring to quiet fusion for 15 to 20 minutes. Avoid rapid heating and explosions. Rotate the melt while solidifying. When cool, put the crucible and cover into a casserole containing 200 cc. of water, add 5 to 10 cc. of bromine water, and boil until the melt is dissolved. Allow to settle, decant, filter and wash through a thick filter with hot water. Cool, acidify the filtrate with dilute hydrochloric acid, using Congo red paper, make up the volume to 400 cc., and precipitate boiling with 10 cc. of a 10 per cent solution of barium chloride, keeping the beaker covered with a watch glass. Allow the precipitate to stand over night, filter on an asbestos mat in a Gooch crucible, wash with hot water, ignite and weigh, cooling in a desiccator. Calculate to sulfur (factor 0.1372), and record as "free sulfur."

ORGANIC ACETONE EXTRACT—When waxy hydrocarbons are not to be determined, subtract the percentage of free sulfur from the percentage of total acetone extract above, and record the difference as "organic acetone extract."

MINERAL FILLERS—Extract a one gram sample as under "acetone extract" above for 4 hours and dry the rubber in the water oven at 95 to 100° C. until the odor of acetone is gone. Transfer the sample to a 100 cc. beaker, burn the thimble to ash, and add the residue to the beaker. Add 50 cc. of clear molten salol, and heat the beaker on the hot plate at a temperature of not less than 120° nor more than 150° C., stirring occasionally until the rubber is apparently dissolved. After settling a few minutes, carefully transfer the liquid to a 200 cc. beaker and examine the residue in the bottom of the smaller beaker for particles of undissolved rubber. If found, more salol is added and solution completed. Stir two cc. of a 1 per

cent solution of soluble cotton in amyl acetate into the united warm liquids in the 200 cc. beaker, cool and add redistilled turpentine until a good "flock" has formed, adding at least 75 cc. of turpentine with constant stirring. Allow the liquid to stand until the flock has settled. The supernatant liquid is decanted and filtered by suction through an alundum crucible (Norton R. A. 84—B. P. 5204) placed in the Spencer holder (E. & A. 1913, No. 2384). Wash the flock by decantation with turpentine, filtering the latter, transfer the whole to the crucible, then dissolve carefully in a few cc. of acetone, and wash the fillers with acetone, being careful not to allow the fillers to cover up the sides of the crucible and so cause clogging. Wash thoroughly all beakers and crucible with acetone, using an acetone extracted policeman. Dry to constant weight at 105° to 110° C., cooling in a desiccator. Evaporate all the filtrates and washings, transfer to a weighed porcelain dish, burn off the organic matter, cool in a desiccator and weigh. Add this weight found to the fillers in the crucible, and calculate and record as "mineral fillers."

TOTAL SULFUR—Mix a five-tenths (0.5) gram sample with six (6) grams of potassium carbonate and four (4) grams of sodium peroxide and proceed exactly as under "free sulfur." Calculate the results in the same manner and record as "total sulfur."

FOREIGN ALCOHOLIC POTASH EXTRACT—When the presence of tar, pitch or asphalt is not indicated, spread out the rubber residue from the acetone extraction and dry in the water oven at 95° to 100° C., until the odor of acetone is no longer apparent. Transfer to a 100 cc. pressure flask (E. & A. 1913, No. 1064), fitted with washers previously extracted with alcoholic potash. Add 50 cc. of alcoholic potash, stopper and heat in an air oven kept between 105° and 110° C. for four hours. Cool the flask, filter and wash the residue with hot absolute alcohol until the washings are no longer colored. Make the filtrate strongly acid with concentrated hydrochloric acid to precipitate potassium chloride, allow to settle, filter and wash with hot chloroform into a small casserole. Place the casserole on the steam bath and evaporate until the odor of hydrochloric acid just disappears. Take up the residue with chloroform, filter and wash with hot chloroform into a beaker, evaporate the chloroform and examine the residue. If the residue is not oily or greasy to the touch, no report shall be made. If the residue is oily or greasy to the touch, it shall be washed with small portions of warm 88° Beaumé naphtha, filtered through a washed plug of cotton into a small weighed beaker, the naphtha evaporated, and the beaker dried in the water oven at 95° to 100° C. in 15-minute periods until the weight is constant, or increases, cooling in a desiccator. Calculate and record as "Foreign Alcoholic Potash Extract."

FOREIGN CHLOROFORM EXTRACT—If the compound is light in color, tar, pitch and asphalt shall be considered absent. If the compound is dark or black in color the residue after the acetone extract determination above, without removing the acetone, and before the alcoholic potash extraction is made, is extracted with chloroform for four hours in the same manner and by the same procedure as for the acetone extraction. If the chloroform extract is very dark in color, or the residue is tarry, from its calculated amount shall be subtracted 3 per cent of the weight of vulcanized rubber gum as determined below, and the balance recorded as "Foreign Chloroform Extract."

PRECAUTIONS—When the chloroform extraction is made the day after the acetone extraction, the rubber residue shall be covered with acetone over night. When the alcoholic potash extraction is made the day after either the acetone extraction or the chloroform extraction, the dried rubber residue shall be covered with the alcoholic potash over night.

CARBONACEOUS FOREIGN MATTER—Heat about a one gram sample with 30 cc. of concentrated nitric acid and 15 cc. water.

is better to specify the amount of the original materials.

The experience of two years has shown proper correspondence of analysis to ingredients used, taking into account changes produced by process of manufacture and vulcanization, when adulterants have not been introduced. The manufacturer cannot take chances with materials of unknown composition under our methods.

In specifications reading "It shall contain," the best evidence that certain materials have been used in the compound is to have an inspector at the factory to see them put in. We think we are safe in saying that rubber manufacturers have had enough of this system. We believe that "It shall show" should be specified, that the methods of analysis and tests should be standardized and the specific items defined. This seems by far the better method and offers fewer opportunities for disputes.

SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME—The physical properties of a rubber compound and the quality are more properly related to the percentage by volume of vulcanized rubber gum present than to the percentage by weight. The large majority of rubber goods are sold by bulk and used by bulk rather than by weight. This volume conception is necessary to an understanding of rubber mixings.

Now the specific gravity of this vulcanized rubber gum (resin-, ash-, and air-free) is very nearly unity. The specific gravity of the purest washed and dried raw rubber is greatly influenced by the mode of preparation in regard to minute air bubbles enclosed in the rubber, and varies from 0.90 to 0.95.

According to Philip E. Young, inventor of Young's Gravitometer, the best value for the pure air-free rubber gum is 0.98. With 30 per cent of combined sulfur without mineral fillers, the specific gravity of the vulcanized rubber gum has been shown to be 1.00. The variation in the specific gravity for various degrees of vulcanization is in any case a small one and for purposes of calculation the specific gravity of all vulcanized rubber gum may be taken as unity. By multiplying the percentage by weight of vulcanized rubber gum present by the specific gravity of the compound a product is obtained which represents the percentage by volume of vulcanized rubber gum present. This volume would be strictly correct if divided by the true specific gravity of the vulcanized rubber gum present. However, it is not intended to determine the true volume, but a factor obtained as specified. As this is very nearly the true volume of vulcanized rubber gum present it has been so called in the methods. No closer method for determining the true volume is possible, or necessary.

It will at once be seen that hard rubbers will show more vulcanized rubber gum by weight than the original rubber put in; and that for soft rubber of good quality that which is taken away and reported as organic acetone extract will about equalize the combined sulfur.

The minimum vulcanized rubber gum by volume

that will give a sound article can hardly be less than 55 per cent if made up of rubber, sulfur and mineral fillers only. Less than this amount needs something to fill the pores between the particles of fillers in the way of resins, oils, waxes or asphaltum. As the percentage of vulcanized rubber gum by volume decreases in a compound made up of rubber, sulfur and mineral fillers only, the liability of decay by oxidation due to porosity becomes greater.

Every manufacturer knows that with a fixed percentage by weight of rubber put into a compound and made into an article with fixed dimensions, like a hose tube or valve, the lighter he can make the specific gravity, the more money he saves. This is due to a reduction in the volume of rubber present. By specifying a minimum percentage by volume of vulcanized rubber gum the choice of fillers is left entirely to the manufacturer, as it should be. Whether he uses light or heavy fillers is immaterial as long as the volume specified is obtained, and the chemical and physical requirements are met. For example, let us suppose a minimum of 75 per cent of vulcanized rubber gum by volume is specified. The manufacturer can meet this by a compound with a specific gravity of 1.22 showing 61.5 per cent vulcanized rubber gum by weight or by a compound with a specific gravity of 2.27 showing 33.0 per cent vulcanized rubber gum by weight, or by various combinations between these extremes. The same result can be obtained by fixing a minimum specific gravity and a minimum percentage by weight of vulcanized rubber gum present but the kind of fillers would then be limited to a few or a mixture of a few having a certain density.

The method specified permits any manufacturer to make as good a compound as he knows how, using good rubber and any fillers he thinks best. He will be on an equal basis of competition with any other manufacturer as far as the quality of the finished article is concerned. He must necessarily also deliver an equal weight of vulcanized rubber gum of quality required to meet the physical tests.

In the few cases where it is advisable to specify total sulfur it is no extra hardship for the manufacturer to specify total sulfur in all forms. It is impracticable to determine sulfur present as barium sulfate, when other forms of barium are present. As a rule, the other chemical and physical tests, including an ageing test, can be made adequate and sufficient to ensure the delivery of goods made up from new rubber. The amounts of sulfur and organic acetone extract are specified as percentages of the weight of vulcanized rubber gum present as they are functions of the amount of rubber present. The specification of fixed limits for these as percentages of the compound does not make due allowance for such corresponding variation of these constituents with the amount of rubber used.

The quality of the rubber used as well as the suitability of the fillers and the proper vulcanization are fixed by physical tests which will be described in an article to follow.

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