DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

No. 62

SOAP

[Third Edition]

JANUARY 24, 1923

PRICE, 5 CENTS

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ABSTRACT.

This circular contains a brief discussion of the general composition of soap and of the most important varieties of soap commonly used, together with an outline of certain manufacturing processes. Detailed specifications, including methods of sampling and testing, are given for special grade laundry soap for use with soft water, hard water grade laundry soap for use in hard water districts, and milled toilet soap for general toilet use. These specifications represent soaps which have very extensive commercial use and are believed to be satisfactory for the grades of soap indicated. They have not been recommended for adoption as Government standards, as there appears to be no demand at this time for soaps of this kind in the Government service. References are given to other circulars of this bureau containing detailed specifications, adopted by the Federal Specifications Board as Government standards, for the following: White floating soap, liquid soap, soap powder, salt-water soap, automobile soap, chip soap, ordinary laundry soap, grit cake soap, scouring compounds, and hand grit soap.

CONTENTS.

I. INTRODUCTION.

This circular contains a brief discussion of the general composition of soap and of the most important varieties of soap commonly used, together with an outline of certain manufacturing procedures. References are made to other circulars containing detailed specifications for the kinds of soap most commonly used by the various branches of the Government, and detailed specifications are given for three varieties of soap that are not at present required by the Government but which are extensively used in some parts of the country.

The bureau has received much valuable assistance in the preparation of this circular from the soap committee of the soap section of the American Specialty Manufacturers' Association, and especially Messrs. A. Campbell and C. P. Long, chairman and secretary of the soap and soap products committee of the American Chemical Society, for which it wishes to express its grateful appreciation.

II. GENERAL COMPOSITION OF SOAP.

All metallic salts of the fatty acids are, strictly speaking, soaps; but the fatty-acid salts of the alkali metals are the only ones that are soluble in water, and therefore the only ones commonly used as cleansers. Soaps of some of the other metals are used for particular purposes, such as aluminum soaps, which are used for thickening lubricating oils and in waterproofing concrete and other materials; iron and chromium soaps, which are used in dyeing and color printing; lead and manganese soaps, which are used as "driers" in paints and varnishes; lime soaps and lead soaps, which are used in the preparation of adhesive plasters; lime soaps, which are used in the preparation of lubricating and axle greases; and magnesium soaps, which are used very extensively in solution in benzol for dry cleaning. These, however, are used for purposes so radically different from those which call for the detergent soaps that they will not be considered in this circular.

In addition to alkali salts of fatty and sometimes rosin acids all soaps contain some water and small amounts of impurities and by-products of manufacture. For various purposes certain other substances ("builders") frequently enter into the composition of commercial soaps. Among building substances may be mentioned sodium carbonate, borate, silicate, and phosphate for

hardening and rendering soaps more detergent when used with hard water; sand, volcanic ash, infusorial earth, pumice, clay, starch, and like substances intended to aid mechanically in the process of cleaning; glycerol, for increasing the emollient properties; sugar, alcohol, and glycerol, for increasing transparency in solid soaps and for preventing clouding and foaming in liquid soaps; colors and perfumes in many varieties. Certain other materials, such as mineral oils, waxes, talc, starch, etc., are sometimes used for specific purposes, but when added for the express purpose of cheapening the soap they should be classified as fillers.

For toilet use or for washing of delicate fabrics in rain water or other very soft water a soap should be used with little or no builders; but with hard waters, or even with soft waters when the fabrics contain greases or are badly soiled, these builders prevent waste and increase the efficiency of soaps by acting as water-softening agents. In all cases the builders tend to increase the detergency of the soap. Certain materials are often added for special purposes. For example, so-called "naphtha soap" contains a special kind of mineral oil; pumice soap contains finely-ground pumice and is used very extensively by mechanics for removing oil and stains fron the hands.

Under special conditions such substances as sulphur, carbolic acid, mercury salts, etc., are added to medicinal soaps. These last, however, are of such a special nature that they will not be considered.

Animal and vegetable fats and oils are mixed esters, or more specifically, mixed glycerides of the higher fatty acids, and it is from these materials that soaps in general are made. The difference between a fat and an oil is mainly physical. The term "fat" is generally applied to those glycerides which are solid at ordinary temperatures and "oil" to those which are liquid under similar conditions. For the sake of simplicity we will use the term "fat" to cover both classes. Each fat as found in nature contains the glycerides of several different fatty acids, the principal ones of which are named, respectively, stearic, palmitic, and oleic acids. These occur in varying quantities in practically all fats, the solid fats containing a large proportion of stearic-acid glyceride (stearin), while the liquid fats contain a large proportion of oleic-acid glyceride (olein). There are a large number of fatty-acid glycerides besides the three mentioned above which occur in certain fats, such as lauric-acid glyceride (laurin) in coconut and palm-

kernel oils, myristic-acid glyceride (myristin) in palm-kernel oil, linoleic-acid glyceride (linolein) in linseed oil, etc.

The numerous animal and vegetable fats, such as tallow, lard, olive oil, palm oil, coconut oil, cottonseed oil, soya-bean oil, etc., are neutral substances which may be decomposed by the aid of superheated steam or other suitable means into two distinct separate portions, namely, a mixture of "fatty acids," on one hand, and "glycerol," on the other.

Saponification is the term applied to this splitting of an ester by the action of water, forming an alcohol and a fatty acid (glycerol is the alcohol in fats). This may be expressed as follows:

Stearin — and water — give glycerol — and stearic acid.

$$C_3H_5(O.\,C_{18}H_{35}O)_3 + 3H_2O = C_3H_5(OH)_3 + 3C_{18}H_{36}O_2$$

The stearic acid can be neutralized by alkali, forming soap, as follows:

Stearic acid — Sodium hydroxide — Water — Sodium stearate soap

$$C_{18}H_{36}O_2 + NaOH = H_2O + C_{18}H_{35}O_2Na$$

It is not necessary to split the fats into glycerol and fatty acid previous to neutralizing the acid with alkali. In fact, one of the most important and one of the oldest methods in use is to treat the fat itself with alkali, the reaction being represented by the equation

Stearin — Sodium hydroxide — Glycerol — Sodium stearate

$$C_3H_5(O.C_{18}H_{35}O)_3 + 3NaOH = C_3H_5(OH)_3 + 3C_{18}H_{35}O_2Na$$

The same type of reaction occurs with all other fats. Mineral and essential oils are not true fats and do not respond to this reaction; in fact, with few exceptions they do not contain fatty acids. Waxes are not glycerides but do contain fatty acids in combination with high molecular-weight alcohols. They can be saponified in the same manner as fats, but are seldom used in this manner.

Rosin (colophony) is an acid substance, and while its exact nature is not as well understood as that of the fats it may be tentatively considered to be mainly abietic acid ($C_{20}H_{30}O_2$), which reacts with alkali according to the equation

$$C_{20}H_{30}O_2 + NaOH = H_2O + C_{20}H_{29}O_2Na.$$

The other subtances mentioned above as occurring in commercial soaps do not constitute a part of the true soaps but are simply admixtures.

Hard soaps are generally soda soaps, while the potash soaps are soft and are more easily soluble than the soda soaps. The character of the fatty materials used also influences the hardness and solubility of the resulting soaps, the hard fats, such as tallow, making harder soaps generally than the more fluid fats. Rosin makes soaps softer, and it can therefore be used best in connection with tallow and other hard fats. Coconut oil and palm-kernel oil make hard soaps, but these soaps dissolve very readily in either hard or soft water, hence lather freely.

The oldest and probably still the best method of soap making is the grained or boiling and settling process. The neutral fats are boiled with caustic alkali until about 90 to 95 per cent saponified. Fatty acids or rosin may be saponified by boiling with carbonated alkali. Salt is then added until the soap is grained or salted out of solution and floats on top as a curdy mass. The salt solution containing glycerol, excess alkali, and other impurities settle to the bottom When properly settled, the salt solution is drawn off as the first "spent lye change." The soap is then thinned out by adding water and sufficient caustic alkali to give it a slightly alkaline reaction after being thoroughly boiled. Salt is again added and the soap grained from the lye. This lye is drawn off as the "second lye change." This process is repeated until the fat is completely saponified and the glycerol and impurities washed out of the soap. These lye changes are used for the recovery of the salt and glycerol. The soap is then boiled with about a 10 to 15 per cent caustic alkali solution to insure complete saponification, and as this strength alkali grains the soap it is allowed to stand after boiling until the soap separates. The lye is then drawn off as the "strong" change

The soap is then thinned with water, boiled to a uniform consistency, and allowed to settle. This settling requires from a few hours to several days, depending on the kind of soap desired. The salt, alkali, and impurities settle to the bottom of the kettle to form the pitch water and nigre, leaving the pure soap on top. In the case of laundry soap the pure soap is then drawn off from the nigre and is "builded" by adding sodium salts, such as carbonate, silicate, borate, etc. Perfumes and any other ingredients required in the completed soap are added at this stage. In the case of toilet and white floating soap, where an extremely neutral soap is desired, the pitch water and nigre are often drawn off and the settling process repeated until the desired neutrality is obtained by settling out the excess of caustic alkali.

The soap maker also uses two other processes known as "cold" and "half" or "semiboiling." In the cold process the melted fat is mixed with strong alkali, and no heat except that of the chemical reaction is required. The half or semiboiling process is similar to the cold process, except that the ingredients are mixed hot. In both of these processes no separation of soap is effected, and the product contains the glycerol and impurities; also the saponification is frequently not completed. The user of soap should bear in mind that there are many varieties of soaps, and what is satisfactory for one purpose may be unsatisfactory or too expensive for another.

III. VARIETIES OF SOAPS.

1. TOILET SOAPS.

Toilet soaps should be entirely neutral, since excess alkali is injurious to the skin. Builders, such as sodium carbonate and sodium silicate, having a similar effect, should also be absent. Free-lathering soap is generally desirable, and since a tallow soap lathers slowly and coconut-oil soap lathers very freely some coconut oil is frequently added. This oil has a tendency to injure the skin, and its odor is also objectionable; hence it is not generally used in large amounts. Some potash is frequently used in toilet soaps to produce freer lathering.

(*a*) MILLED TOILET SOAPS are prepared by first obtaining a finely divided (flake or powder), pure, dry soap, adding perfume, if desired and compressing into cakes. More delicate perfumes can be used with this class of soaps, since the perfume is mixed in the process of milling, than with ordinary soaps in which the perfume is added before the soap is dried.

A common method of manufacturing such soaps consists in running the soap while liquid over cooling rolls, chilling, and then scraping off in the form of thin ribbons or flakes. These are dried to reduce the moisture content to 12 to 15 per cent and then run with the perfume and any added filler through heavy mixers or mixing rolls. The soap when homogeneous is put through a special mixer, called a plodder, which forces it out in a shape for cutting into bars or cakes.

(*b*) FLOATING SOAPS contain entangled air in very fine bubbles, incorporated while the soap is still hot. These air bubbles are so small as to be almost invisible and so numerous that they not only make the soap lighter than water but also largely increase the surface of the soap exposed to water when used, and therefore

render it more quickly soluble than the same soap would be without the bubbles.

(*c*) CASTILE SOAP was originally made from low-grade olive oils. The name now represents a type of soap, the term "castile" being applied to a soap intended for toilet or household use, sold usually in large, unwrapped, unperfumed bars, which are cut up when sold or when used. It is often drawn directly from the kettle without "crutching,"[1] but is sometimes crutched a little or even enough to make it float and is sometimes milled. It is also sold in small bars both wrapped and unwrapped. The type is not one easily defined, so now when made from olive oil it is invariably sold as olive-oil castile. There are soaps made entirely from coconut oil which are sold as coconut castiles or hard-water castiles. Many other castiles are made from a mixture of coconut oil and tallow.

(*d*) TRANSPARENT SOAPS were originally made by dissolving soap in alcohol and filtering. The transparency formerly was considered an indication of freedom from impurities, but the same effect can be produced in other ways, and the transparency is actually no indication whatever of purity or quality.

(*e*) LIQUID SOAPS are water solutions generally of a neutral coconut-oil potash soap, containing glycerol, sugar, or alcohol added to prevent cloudiness and foaming in the container. The glycerol is probably an unobjectionable addition, since it has emollient properties, but sugar can have no beneficial action on the soap itself and may be objected to on account of its tendency to leave the hands sticky. Alcohol is seldom used.

(*f*) SHAVING SOAPS must possess not only the properties of first-class toilet soaps, but must furnish a very copious lather, which will remain on the face for some time without drying. This lather should soften the beard without injuring the skin. These soaps should have no unpleasant odor and little or no perfume. The fat used in shaving soaps generally contains some coconut oil, and the alkali is generally a mixture of soda and potash. Glycerol is also generally present.

2. SALT-WATER SOAP.

Soap for use on ocean-going vessels is soda soap, made entirely of coconut oil, with frequently a small amount of sodium carbonate as a filler. It is less easily precipitated by salt water than soaps made from other fats.

[1] A "crutcher" is a mixing machine which derives its name from the early soap factories. Mixing was then done by hand with a wooden stick shaped like a crutch.

3. LAUNDRY OR COMMON SOAPS.

(*a*) LAUNDRY CAKE SOAP is probably used in larger quantities than any other. Ordinary laundry soap is generally made of soda and tallow, with some rosin. The tallow is frequently replaced partly or wholly by grease, cottonseed, coconut, and palm-kernel oils, or hydrogenated fish and vegetable oils. Rosin is added to increase the lathering qualities of the soap and is an aid in this respect when used up to not exceeding one-third of the total fat. Large amounts tend to make the soap sticky and too soluble and tend to harden the fabric washed with it. Sodium carbonate is added to the soap to increase its water-softening and detergent properties where it is to be used with hard waters.

Sodium silicate is also added to soaps to increase their detergent and water-softening properties, especially where the soaps contain 20 to 30 per cent of coconut oil and are intended for use in hard-water districts. Borax and sodium phosphate have similar action to sodium carbonate and sodium silicate.

(*b*) CHIP SOAPS designed for laundry purposes are generally made from tallow, greases, or hydrogenated fish or vegetable oils combined with soda. Chip soaps for textile use usually contain some olive or palm oil, also oleic acid. Chip soaps designed for fine laundry use, such as washing of laces and fine fabrics, usually contain a considerable amount of coconut oil. Chip soaps are made by running the liquid soap over cooling rolls, which reduce the soap to a thin ribbon.

These ribbons are passed through dryers, which reduce the moisture content to about 10 to 15 per cent, after which the soap is either run through granite calender rolls which reduce it to thin flakes or chips or through disintegrators which pulverize it to a fine powder. Modern laundry practice demands a soap that will dissolve quickly when added directly to the wheel instead of being made, as was formerly the case, into a soft soap with the addition of soda ash. The reason for this is that the soft soap has a tendency to separate in the tank into layers, making exact measurement difficult, while the fine flakes or powders can be added in definite quantities. Chip soap should be free from objectionable odor and should contain no rosin. It also should rinse readily from the garment, so as to prevent precipitation of fatty acids causing soap specks when the acid bleach is added after the rinsing has been completed.

4. SOAP POWDERS.

A soap powder (not to be confused with "powdered chip soap" mentioned above) should be entirely soluble in water and should consist of powdered soap and sodium carbonate. Soap powders usually contain 15 to 20 per cent of anhydrous soap and the balance of crystallized sodium carbonate, often with the addition of borax, sodium phosphate, etc. They are used very extensively for general household work owing to their ease of application, solubility, and cleansing qualities.

5. SCOURING POWDERS.

A scouring powder should consist of a mixture of soap powder and an insoluable abrasive. The abrasive is usually powdered pumice, volcanic ash, quartz, marble, or feldspar.

6. SCOURING CAKES.

Scouring cakes consist largely of abrasive material, such as sand, powdered pumice, volcanic ash, etc., with a binder of soap, and frequently considerable sodium carbonate

7. AUTOMOBILE SOAPS.

Automobile soap is a paste soap made from vegetable oils of low titer, other than coconut oil, combined with soda or potash or a mixture of soda and potash, and frequently contains a smal excess of neutral fat.

IV. SPECIFICATIONS.

Large consumers, such as the various branches of the Government service, municipalities, etc., have for many years purchased various kinds of soap under definite specifications, but an examination of such existing specifications shows a great variety of requirements for the same kind of soap.

Hard water is being used more and more for household laundry purposes. The use of rain water from barrels, cisterns, and streams is being supplanted by water from deep wells and from rivers and lakes, which has been rendered hard by purification with alum and lime. To meet this changing condition, soap manufacturers have been called upon to manufacture a soap that will lather freely in these hard waters. They met the situation by increasing the alkaline builders in the yellow laundry soaps and by substituting coconut oil for rosin and producing the so-called white laundry soaps. The alkaline builders are

usually added in the crystallized form; that is, they are in solution in what is equivalent to their water of crystallization and when allowed to cool will crystallize in the soap to a solid state. These builders usually contain about 35 per cent of the alkaline salt and 65 per cent of water of crystallization. The addition of these alkaline builders in increased quantities to laundry soaps has increased the water content of these soaps. The pure soaps free from builders contained 28 to 30 per cent of moisture, while the yellow laundry soaps when builded contain 36 to 38 per cent of moisture, and the white laundry soaps 38 to 42 per cent of moisture.

Purchasing soap products under specifications necessitates sampling and testing, which are costly operations; hence it is only advisable to purchase under specifications when the amounts delivered are large. When the amounts purchased are small, it is more economical to pay a high price for a brand desired than to incur the expense of testing a product offered at a low price.

It would be of distinct advantage to both manufacturers and consumers if one specification for any particular type of soap could be generally used by a large number of consumers. Such a specification should secure a soap suitable for the intended use but, as far as possible, admit material of regular commercial makes. It should allow the greatest freedom in the selection of stock that is consistent with quality, so that the manufacturer can take advantage of both varying market conditions and advances in technology of fats and oils and thus prevent, as far as possible, excessive prices due to temporary scarcity in any specific raw material. Methods of sampling and testing should be clearly defined and be made a part of the specification.

Below is given a list of specifications published as separate circulars of this bureau. In preparing these specifications conferences were held first with representatives of many branches of the Government service, for the needs of these departments were considered as fairly representing those of the general public. A tentative set of specifications was submitted to a large number of manufacturers for criticism and suggestion. From the conflicting and divergent statements contained in the replies of the various manufacturers it became apparent that the matter could be best handled by a technical committee representing the manufacturers and a similar committee representing the Government. The manufacturers were requested to designate such a committee

to confer with a Government committee for the purpose of preparing specifications that would give material of suitable quality to cover the general needs of the Government service and at the same time conform to commercial practice. In the meantime the Federal Specifications Board appointed a technical committee on soap. This committee took up the matter of soap specifications and held a conference with a technical committee of the soap section of the American Specialty Manufacturers' Association, said to directly represent more than 90 per cent of the soap manufacturers of the country. As a result of this conference specifications were prepared by the two technical committees and submitted to the Federal Specifications Board and by it adopted as Government standards. The methods of sampling and analysis given in the various specifications referred to and in this circular are those recommended by the soap and soap products committee of the American Chemical Society and were prepared by this committee in cooperation with the two technical committees mentioned above.

The following U. S. Government specifications for soaps have been published as separate circulars of the Bureau of Standards:

White floating soap. (See B. S. Circular No. 123.)

Liquid soap. (See B. S. Circular No. 124.)

Soap powder. (See B. S. Circular No. 125.)

Salt-water soap. (See B. S. Circular No. 126.)

Automobile soap. (See B. S. Circular No. 127.)

Chip soap. (See B. S. Circular No. 128.)

Ordinary laundry soap. (See B. S. Circular No. 129.)

Grit cake soap (*a*) and (*b*). (See B. S. Circular No. 130.)

Scouring compounds. For floors (*a*) and (*b*) and soap compound (*c*). (See B. S. Circular No. 131.)

Hand grit soap. (See B. S. Circular No. 132.)

V. APPENDIXES.

The following appendixes give additional specifications for special grade laundry soap, hard water grade laundry soap, and milled toilet soap. They were submitted by the manufacturers' committee and represent soaps which have very extensive commercial use and are believed to be satisfactory for the grades of soap indicated. These specifications have not been recommended for adoption as Government standard, as there appears to be no demand at this time for soaps of this kind in the Government service.

APPENDIX 1.—PROPOSED SPECIFICATION FOR SPECIAL GRADE LAUNDRY SOAP.

1. GENERAL.

The soap desired under this specification is a high-grade, well-made, uniformly mixed laundry soap, made from soda and fats, free from or with only a relatively small proportion of rosin, low in matter insoluble in alcohol, free from objectionable odor, and suitable for use with soft water for general cleaning and laundry purposes. Bidder shall state size, weight, and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 34 per cent. Deliveries which yield more than 34 per cent of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 5 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.2 per cent.

Matter insoluble in water shall not exceed 1.0 per cent.

Rosin shall not exceed 20 per cent.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 30 per cent of matter volatile at 105° C.

The material will be purchased by net weight, provided the matter volatile at 105° C. does not exceed 30 per cent. With deliveries containing more than 30 per cent, but not exceeding 34 per cent of matter volatile at 105° C., settlement will be made on the basis of 30 per cent of matter volatile at 105° C.; that is, seven-tenths of a pound of nonvolatile matter shall be considered 1 pound of soap.

Examples: (1) Yield 28 per cent of matter volatile at 105° C., pay for net weight.

(2) Yield 33 per cent of matter volatile at 105° C., percentage of net weight to be paid for is calculated as follows: $(100-33)\times 10/7=95.71$ per cent.

2. SAMPLING.

One cake shall be taken at random from not less than 1 per cent of the vendor's shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers a cake shall be taken at random from each lot of containers

totaling not to exceed 5,000 pounds. The total sample shall in all cases consist of not less than three cakes taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds.

Wrap the individual cakes tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped cake, record its weight and the date of weighing on the wrapper, place the wrapped cakes in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested. The seller shall have the option of being represented at the time of sampling, and, when he so requests, shall be furnished with a duplicate sample.

3. LABORATORY EXAMINATION.

(*a*) PREPARATION OF SAMPLE.—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that can not be handled as above, select a cake of average weight, quarter by cutting at right angles in the center, and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an air-tight container in a cool place. When a determination shows nonconformity with specification, a duplicate shall be run.

(*b*) MATTER VOLATILE AT 105° C.—Weigh 5 g of the sample in a porcelain or glass dish about 6 to 7 cm in diameter and 4 cm deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105° C.[2] Report loss in weight as matter volatile at 105° C.

(*c*) TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID.—(1) *Matter insoluble in alcohol.*—Digest hot a 10 g sample with 200 cc of freshly boiled neutral ethyl alcohol (94 per cent or higher). Filter through a counterpoised filter paper, neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper or in the

[2] Time can be saved by having a layer of about 3 mm of ignited sand and a small stirring rod weighed with the dish and dissolving the sample in absolute alcohol, evaporating to dryness, breaking up the sample with the rod, adding more alcohol, again evaporating, and completing the drying in the oven as above.

crucible with hot neutral alcohol until free from soap. Dry the filter paper or crucible and residue at 100 to 105° C. for three hours, cool, and weigh the total matter insoluble in alcohol.

(2) *Free alkali or free acid.*—Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution and calculate the alkalinity to sodium hydroxide or acidity to oleic acid.

(3) *Matter insoluble in water.*—Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue extract it with water at 60° C. and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100 to 105° C. for three hours, cool, and weigh matter insoluble in water. The nature of this may be determined by further examination.

(*d*) CHLORIDE.[3]—Dissolve 5 g of the sample in 300 cc of water, boiling, if necessary, to effect solution of all soluble matter. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc of a 20 per cent $Mg(NO_3)_2 . 6H_2O$ solution). Without cooling or filtering titrate with standard silver nitrate solution, using potassium chromate as indicator. Calculate the chloride as sodium chloride.

(*e*) ROSIN.—Wolff's method.[4] Dissolve 5 g of the sample in 100 to 200 cc of hot water, add a slight excess of dilute sulphuric acid, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small portion of ether, draw off the water layer, and wash the ether solution with water until free from mineral acid. Transfer to a 200 cc Erlenmeyer flask, evaporate off the ether and dry one hour at 105° C., cool, and dissolve in 20 cc of absolute alcohol. Then add 10 cc of a solution of one volume of concentrated sulphuric acid (sp. gr. 1.84) and four volumes of absolute alcohol and boil for four minutes under a reflux condenser. Remove from steam bath and add to the liquid about five times its volume of 7 to 10 per cent sodium chloride solution and extract with ether. Shake out the aqueous portion two or three times with ether. Unite the ether solutions and wash with sodium chloride solution until the washings are neutral to methyl-orange. Add 30 cc of neutral alcohol and titrate the rosin acids with standard sodium hydroxide solution, using phenolphthalein as indicator. Calculate to rosin or rosin soap, as desired (1 cc normal alkali = 0.346 g rosin or 0.377 g rosin soda soap).

[3] H. C. Bennet, J. Ind. Eng. Chem., 13, p. 813; 1921.

[4] Chem. Ztg. 38, pp. 369–370, 382–383, 430; Chem. Abstr. 8, p. 2495; 1914.

4. REAGENTS.

(*a*) STANDARD SODIUM HYDROXIDE SOLUTION.—0.25 N or about 10 g of sodium hydroxide dissolved in water and diluted to 1 liter. Standardized against Bureau of Standards benzoic acid.

(*b*) STANDARD SULPHURIC ACID SOLUTION.—0.5 N or about 25.8 g of concentrated sulphuric acid (sp. gr. = 1.84) diluted to 1 liter. Standardized against standard sodium hydroxide solution (*a*).

(*c*) STANDARD SILVER NITRATE SOLUTION.—0.10 N or about 17 g of silver nitrate dissolved in water and diluted to 1 liter. Standardized against pure sodium chloride.

(*d*) POTASSIUM CHROMATE SOLUTION.—A 10 per cent solution of potassium chromate (K_2CrO_4) in water.

APPENDIX 2.—PROPOSED SPECIFICATION FOR HARD WATER GRADE LAUNDRY SOAP.

1. GENERAL.

The soap desired under this specification is a well-made uniformly mixed laundry soap, made from soda and fats, of which not less than 20 per cent shall be coconut oil; free from rosin, free from objectionable odor and suitable for use with hard water for general cleaning and laundry purposes. Bidder shall state size, weight, and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Color to match that of sample submitted for color only.

Matter volatile at 105° C. shall not exceed 44 per cent.

Deliveries which yield more than 44 per cent of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall be not less than 8 per cent nor more than 20 per cent.

Free alkali, calculated as sodium hydroxide (NaO H), shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 1.0 per cent.

The acid number of the mixed fatty acids prepared from the soap shall be not less than 205.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 38 per cent of matter volatile at 105° C.

The material will be purchased by net weight, provided the matter volatile at 105° C. does not exceed 40 per cent. With deliveries containing more than 40 per cent, but not exceeding 44 per cent of matter volatile at 105° C., settlement will be made on the basis of 40 per cent of matter volatile at 105° C.; that is, six-tenths of a pound of nonvolatile matter shall be considered 1 pound of soap.

Examples: (1) Yield 39 per cent of matter volatile at 105° C., pay for net weight.

(2) Yield 42 per cent of matter volatile at 105° C., percentage of net weight to be paid for is calculated as follows: $(100-42)\times\frac{10}{6}=96.67$ per cent.

2. SAMPLING.

One cake shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers a cake shall be taken at random from each lot of containers totaling not to exceed 5,000 pounds. The total sample shall in all cases consist of not less than three cakes taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds.

Wrap the individual cakes tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped cake, record its weight and the date of weighing on the wrapper, place the wrapped cakes in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested. The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

3. LABORATORY EXAMINATION.

(*a*) PREPARATION OF SAMPLE.—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large each cake may be quartered and one-quarter of each cake run through the chopper. With samples that can not be handled as above, select a cake of average weight, quarter by cutting at right angles in the center, and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions

for analysis promptly. Preserve the remainder in an air-tight container in a cool place. When a determination shows nonconformity with specification, a duplicate shall be run.

(*b*) MATTER VOLATILE AT 105° C.—Weigh 5 g of the sample in a porcelain or glass dish about 6 to 7 cm in diameter and 4 cm deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105° C.[5] Report loss in weight as matter volatile at 105° C.

(*c*) TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID.—(1) *Matter insoluble in alcohol.*—Digest hot a 10 g sample with 200 cc of freshly boiled neutral ethyl alcohol (94 per cent or higher). Filter through a counterpoised filter paper, neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper or in the crucible with hot neutral alcohol until free from soap. Dry the filter paper or crucible and residue at 100 to 105° C. for three hours, cool, and weigh the total matter insoluble in alcohol.

(2) *Free alkali or free acid.*—Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution and calculate the alkalinity to sodium hydroxide or acidity to oleic acid.

(3) *Matter insoluble in water.*—Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue extract it with water at 60° C. and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100 to 105° C. for three hours, cool, and weigh matter insoluble in water. The nature of this may be determined by further examination.

(*d*) CHLORIDE.[6]—Dissolve 5 g of the sample in 300 cc of water, boiling, if necessary, to effect solution of all soluble matter. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc of a 20 per cent $Mg(NO_3)_2.6H_2O$ solution). Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator. Calculate the chloride as sodium chloride.

(*e*) ACID NUMBER.—(1) *Preparation of fatty acids.*—Dissolve about 50 g of the soap in 300 cc of hot water, transfer to a sepa-

[5] Time can be saved by having a layer of about 3 mm of ignited sand and a small stirring rod weighed with the dish and dissolving the sample in the absolute alcohol, evaporating to dryness, breaking up the sample with the rod, adding more alcohol, again evaporating, and completing the drying in the oven as above.

[6] H. C. Bennet, J. Ind. Eng. Chem., 13, p. 813; 1921.

ratory funnel, add 150 cc of approximately 2N H_2SO_4, cool somewhat, add 120 cc of ether, shake, draw off the acid layer, and wash the ether layer free from mineral acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 g of anhydrous sodium sulphate (Na_2SO_4), stopper the flask, shake, and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulphate. Filter through a dry paper into another Erlenmeyer flask and completely evaporate off the ether by passing through the flask a current of dry air while heating the flask to a temperature not above 50° C.

(2) *Determination.*—In a 250 cc Erlenmeyer flask dissolve about 2 g of the fatty acids, accurately weighed, in 20 to 30 cc of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mg of KOH per g of fatty acids).

(*f*) ROSIN.—A qualitative test for rosin may be made as follows: After decomposing a solution of the soap and separating the fatty acids heat a small quantity of the latter with acetic anhydride, cool, place a few drops on a spot plate and add a drop of H_2SO_4 (sp. gr. 1.53). A fugitive violet color indicates the presence of rosin.

4. REAGENTS.

(*a*) STANDARD SODIUM HYDROXIDE SOLUTION.—0.25 N or about 10 g of sodium hydroxide dissolved in water and diluted to 1 liter. Standardized against Bureau of Standards benzoic acid.

(*b*) STANDARD SULPHURIC ACID SOLUTION.—0.5 N or about 25.8 g of concentrated sulphuric acid (sp. gr. = 1.84) diluted to 1 liter. Standardized against standard sodium hydroxide solution (*a*).

(*c*) STANDARD SILVER NITRATE SOLUTION.—0.10 N or about 17 g of silver nitrate dissolved in water and diluted to 1 liter. Standardized against pure sodium chloride.

(*d*) POTASSIUM CHROMATE SOLUTION.—A 10 per cent solution of potassium chromate (K_2CrO_4) in water.

(*e*) SULPHURIC ACID (SP. GR. = 1.53).—Mix 62.5 cc of strong sulphuric acid (sp. gr. = 1.84) with 61.5 cc of water.

(*f*) STANDARD ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Same as (*a*), excepting that ethyl alcohol (94 per cent or higher) is used instead of water.

APPENDIX 3.—PROPOSED SPECIFICATION FOR MILLED TOILET SOAP.

1. GENERAL.

The soap desired under this specification is a high grade, milled cake soap, as free as possible from water, either colored or uncolored and unscented or perfumed in a manner indicated in the contract, thoroughly saponified, well compressed in firm, smooth cakes of a size and shape specified in the contract. It should lather freely when used with cold water. Bidder shall state weight and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 15 per cent. Deliveries which yield more than 15 per cent of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 1.5 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1 per cent.

Matter insoluble in water shall not exceed 0.1 per cent.

Unsaponified saponifiable matter shall not exceed 0.1 per cent.

Rosin, sugar, and foreign matter shall not be present.

The color, odor, and character of the soap must be as specified by the purchaser.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 15 per cent of matter volatile at 105° C.

The material will be purchased by net weight.

2. SAMPLING.

One cake shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds each. In the case of smaller containers, a cake shall be taken at random from each lot of containers totaling not to exceed 5,000 pounds. The total sample shall in all cases consist of not less than three cakes taken at random from separate containers. With very large lots, where the sample drawn as above will amount to more than 20 pounds, the percentage of packages sampled shall be reduced, so that the amount drawn shall not exceed 20 pounds.

Wrap the individual cakes tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector should accurately weigh each wrapped cake, record its weight and

the date of weighing on the wrapper, place the wrapped cakes in an air-tight container, which should be nearly filled, seal, mark, and send to the laboratory for test. Samples should be kept cool until tested. The seller shall have the option of being represented at the time of sampling and when he so requests shall be furnished with a duplicate sample.

3. LABORATORY EXAMINATION.

(*a*) PREPARATION OF SAMPLE.—In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large each cake may be quartered and one-quarter of each cake run through the chopper. With samples that can not be handled as above, select a cake of average weight, quarter by cutting at right angles in the center, and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an air-tight container in a cool place. When a determination shows nonconformity with specification, a duplicate shall be run.

(*b*) MATTER VOLATILE AT 105° C.—Weigh 5 g of the sample in a porcelain or glass dish about 6 to 7 cm in diameter and 4 cm deep, dry to constant weight in an inert atmosphere at a temperature not exceeding 105° C.[7] Report loss in weight as matter volatile at 105° C.

(*c*) TOTAL MATTER INSOLUBLE IN ALCOHOL. FREE ALKALI OR FREE ACID.—(1) *Matter insoluble in alcohol.*—Digest hot a 10 g sample with 200 cc of freshly boiled neutral ethyl alcohol (94 per cent or higher). Filter through a counterpoised filter paper, neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper or in the crucible with hot neutral alcohol until free from soap. Dry the filter paper or crucible and residue at 100 to 105° C. for three hours; cool and weigh the total matter insoluble in alcohol.

(2) *Free alkali or free acid.*—Titrate the filtrate from the above, using phenolphthalein as indicator, with standard acid or alkali solution and calculate the alkalinity to sodium hydroxide or acidity to oleic acid.

(3) *Matter insoluble in water.*—Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue extract it with water at 60° C. and wash

[7] Time can be saved by having a layer of about 3 mm of ignited sand and a small stirring rod weighed with the dish and dissolving the sample in absolute alcohol, evaporating to dryness, breaking up the sample with the rod, adding more alcohol, again evaporating and completing the drying in the oven as above.

the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Dry the filter and residue at 100 to 105° C. for three hours, cool, and weigh matter insoluble in water. The nature of this may be determined by further examination.

(*d*) CHLORIDE.[8]—Dissolve 5 g of the sample in 300 cc of water, boiling, if necessary, to effect solution of all soluble matter. Add an excess of neutral, chlorine-free magnesium nitrate solution (about 25 cc of a 20 per cent $Mg(NO_3)_2 . 6H_2O$ solution). Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator. Calculate the chloride as sodium chloride.

(*e*) UNSAPONIFIED SAPONIFIABLE MATTER.—Weigh 5 g of the soap into a beaker and dissolve in about 100 cc of 50 per cent alcohol on the steam bath. If the sample has been found to contain free fatty acid, add just enough aqueous alkali to neutralize this. Evaporate off the bulk of the alcohol; take up with about 200 cc of hot water, and transfer to a separatory funnel of about 500 cc capacity, designated as No. 1. When cool, rinse out the beaker with about 50 cc of ether and add it to the soap solution. Shake thoroughly for one minute. By the addition of small amounts of alcohol (5 cc portions and the total not to exceed 25 cc) a clear and rapid separation of the aqueous and ether layers is effected. After adding each alcohol portion the separatory funnel is not shaken, but merely given a whirling movement. Draw off the aqueous portion into another separatory funnel, designated as No. 2. Wash the ether solution with 10 cc portions of water until this water is no longer alkaline to phenolphthalein. Add all of these washings to funnel No. 2 and extract this solution with 20 cc portions of ether until the ether is absolutely colorless (three or four extractions should be sufficient). Combine these ether extracts in a third separatory funnel (No. 3) and wash with 10 cc portions of water until the water is no longer alkaline to phenolphthalein. Now add the ether in funnel No. 3 to that in funnel No. 1, a small amount of ether being used to rinse out funnel No. 3. Wash the ether solution with 20 cc of 10 per cent hydrochloric-acid solution and then successively with 20 cc portions of water until the water is no longer acid to methyl orange. Filter the ether solution through a dry filter paper into a weighed beaker or flask. Evaporate or distil off the ether on the steam bath, dry as under the determination of matter volatile at 105° C., and weigh the residue. Then heat with alcohol and, when cool, neutralize with standard alkali,

[8] H. C. Bennet, J. Ind. Eng. Chem., 13, p. 813; 1921.

using phenolphthalein. Deduct any appreciable amount of fatty acid found by this titration from the weight of the residue. This residue consists of the unsaponifiable matter and any neutral fat that may have been present in the soap. Thoroughly saponify the residue with alcoholic alkali and repeat the above procedure. The residue obtained is unsaponifiable matter only, and its weight deducted from that of the residue before saponification gives the weight of unsaponified saponifiable matter.

(*f*) ROSIN.—A qualitative test for rosin may be made as follows: After decomposing a solution of the soap and separating the fatty acids heat a small quantity of the latter with acetic anhydride, cool, place a few drops on a spot plate, and add a drop of H_2SO_4 (sp. gr. = 1.53). A fugitive violet color indicates the presence of rosin.

(*g*) SUGAR.—A qualitative test for sugar may be made as follows: Add a decided excess of hydrochloric acid to a solution of the soap, heat on a steam bath for 15 minutes, cool, filter from fatty acids, and test a portion of the filtrate, which has been neutralized with sodium hydroxide solution, by boiling for two minutes with an equal volume of boiling Fehling's solution. The formation of red cuprous oxide indicates the presence of sugar.

4. REAGENTS.

(*a*) STANDARD SODIUM HYDROXIDE SOLUTION.—0.25 N or about 10 g of sodium hydroxide dissolved in water and diluted to 1 liter. Standardized against Bureau of Standards benzoic acid

(*b*) STANDARD SULPHURIC ACID SOLUTION.—0.5 N or about 25.8 g of concentrated sulphuric acid (sp. gr. = 1.84) diluted to 1 liter. Standardized against standard sodium hydroxide solution (*a*).

(*c*) STANDARD SILVER NITRATE SOLUTION.—0.10 N or about 17 g of silver nitrate dissolved in water and diluted to 1 liter. Standardized against pure sodium chloride.

(*d*) POTASSIUM CHROMATE SOLUTION.—A 10 per cent solution of potassium chromate (K_2CrO_4) in water.

(*e*) SULPHURIC ACID (SP. GR. = 1.53).—Mix 62.5 cc of strong sulphuric acid (sp. gr. = 1.84) with 61.5 cc of water.

(*f*) FEHLING'S SOLUTION.—(1) *Copper sulphate solution.*—Dissolve 34.639 g of copper sulphate ($CuSO_4.5H_2O$) in water and dilute to 500 cc.

(2) *Alkaline tartrate solution.*—Dissolve 173 g of Rochelle salts ($NaKC_4H_4O_6.4H_2O$) and 50 g of sodium hydroxide in water and dilute to 500 cc. Mix equal volumes of (1) and (2) immediately before use.