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DETERGENT COMPOSITIONS

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The present invention relates to detergent compositions.

It is an object of the present invention to provide detergent compositions having improved washing effects without the production of substantial amounts of foam. It is a further object to prepare detergent compositions stable to alkali.

Compositions such as herein-disclosed are particularly adapted for use in automatic washing machines especially in the closed type of washer because of the above-mentioned almost total absence of suds. It has been found that the use of the ordinary sudsing type of detergent in such machines results in a somewhat decreased efficiency due to the mechanical blanketing of the drop of the clothes by the excess amount of suds. Moreover, due to the markedly reduced tendency to foam of the present detergents, it is possible to increase the speed of the agitator or spinner resulting in an increase in the efficiency of the extraction of the wash water.

The present compositions, in which the parts are by weight, are produced by reacting abietic acid or products containing the same, such as rosin, rosin oil, or tall oil with ethylene oxide in amount such that at least 0.5 part, but less than 2.3 parts, of ethylene oxide per part thereof are condensed and the condensation product thus obtained combined with from 20 to 50 parts of a phosphate salt selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium phosphate and sodium hexametaphosphate and mixtures thereof, and the balance to make 100 parts of a carbohydrate material selected from the class consisting of starch and carboxymethylcellulose and mixtures thereof.

Tall oil is obtained as a by-product in large quantities in the paper industry, wherein paper pulp is produced by the sulfate process; the major constituents of the oil comprise rosin acids, fatty acids and certain non-acid constituents, chiefly sterols and the like. The composition of tall oil is somewhat variable; however, it usually has a composition within the following limits:

	Per cent
Fatty acids-----	30-45
Rosin acids-----	50-55
Non-acids-----	8-10

In some cases the rosin acids or abietic acid may be crystallized or separated out of the tall oil and a fraction consisting largely of Steele's abietic acid containing smaller amounts of fatty acids than normally present in tall oil obtained.

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Such a fraction may contain from 0.5% to 15% or 28% of free fatty acids, the balance being abietic acid and as such may be employed for the production of the herein-described products.

In some cases it may be desirable to remove part of the rosin acids from the tall oil, thus obtaining a tall oil containing a higher percentage of fatty acids than normally occurs therein. If desired, the non-acids, namely, the sterols, and other unsaponifiables, may be removed from the tall oil prior to condensation with ethylene oxide.

Still another rosin-containing product which may be employed is the rosin oil of commerce. It is obtainable in various grades containing varying amounts of abietic acid together with terpenes resulting from the decarboxylation of abietic acid by means of heat. The grade known as "kidney oil" has been found to be suitable. Any rosin oil containing from 56% of abietic acid to as little as 25% of abietic acid may be employed.

Prior known products produced by the condensation of fatty acids containing at least 6 carbon atoms, such as stearic, oleic, or ricinoleic acids with ethylene oxide, the ethylene oxide being employed in amount such that at least four ethenoxy groups were condensed per mole of acid, have been characterized as possessing excellent foaming properties. It was, accordingly, expected that the tall oil-ethylene oxide condensation products, because of the presence therein of large quantities of fatty acids, would also show foaming properties. This, however, was not the case. Not only have we discovered that the rosin-ethylene oxide condensation product was free of any tendency to foam, but even the products made from tall oil and hence containing substantial percentages of fatty acids in addition to abietic acid were also surprisingly free of suds-producing properties. We have also found that the foaming tendency is not increased by the use of alkali metal phosphates which are ordinarily regarded as foam promoters. The presence of an alkali metal phosphate, particularly sodium phosphate, not only greatly increases the detergent efficiency of the condensation product, but also produces a material of improved physical properties.

The physical properties of the condensation products produced from tall oil or rosin depend upon the amount of ethylene oxide combined therewith. The tall oil-ethylene oxide product at room temperature is a readily flowing, sticky oil in the lower ranges of combined ethylene oxide, becoming more viscous as the amount of

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ethylene oxide is increased and finally reaching a consistency equivalent to that of a soft wax as the combined ethylene oxide reaches 2 parts per part of tall oil.

The rosin-ethylene oxide product is an oily liquid having approximately the same fluidity as the tall oil product. As the ethylene oxide content of the product is increased it becomes somewhat more viscous. However, we have not observed any tendency to become semi-solid or wax-like in the higher ranges.

Physical properties above-described are such that the condensation product cannot usually be conveniently employed for domestic purposes as such, for such purposes the product is desirably produced in the form of a mixture with finely divided sodium phosphates and carbohydrate materials.

The present detergent compositions are produced by mixing an alkali metal, preferably sodium, phosphate salt with the condensation product obtained by reacting rosin, rosin oil, or tall oil or other abietic acid-containing products with gaseous ethylene oxide until between 0.5 part but less than 2.3 parts by weight of ethylene oxide have been combined with each part of rosin or tall oil.

The condensation reaction of ethylene oxide with tall oil may be carried out at any temperature above the melting or solidification point of the material treated. Generally, a temperature above 130° C., but below 190° C. is suitable for tall oil or rosin or rosin oil. The products so obtained are mixed in any desired manner with sodium phosphates and carbohydrate materials as above-described.

The evaluation of the products herein-described is made by means of the standard Launderometer procedure. This procedure is described by Jay C. Harris in Soap and Sanitary Chemicals for August and September, 1943. The "hard" water employed in the test had a hardness of 300 p. p. m., the "soft" water had a hardness of 50 p. p. m. The detergent was employed in a concentration of 0.2%. However, instead of reporting the results in percentage of soil removed, as described in the above article, the percentage of soil removed is compared with the percentage of soil removed by a standard detergent. For this purpose, Gardinol WA (the sodium sulfate of cocoanut oil alcohols) was employed as the standard detergent and the soil removed by this material was taken as 100%. Accordingly, the detergency results herein reported are referred to as "relative" detergency, it being understood that a comparison with the standard material is made.

The following examples are illustrative of our invention:

Example 1

100 g. of rosin was melted and then heated to a temperature between 150° C. and 160° C. 0.5 g. of potassium hydroxide was added. Ethylene oxide gas was passed into the molten rosin until 73 g. had combined with the rosin. Approximately 5 moles of ethylene oxide per mole of abietic acid had been combined. The product was partly water-soluble, producing a turbid solution and was stable to alkalis.

The product, when tested for detergency according to the standard Launderometer procedure mentioned above, showed a relative detergency of 21.5% in soft water and 13.6% in hard water. The product was a somewhat viscous, sticky oil at room temperature.

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This product was then mixed with tetrasodium pyrophosphate and starch in the proportions by weight of 20 parts of the above condensation product, 40 parts of finely divided tetrasodium pyrophosphate and 40 parts of corn starch. The product was a dry, non-sticky powder of good flowability.

The above combination of the rosin-ethylene oxide condensation product, tetrasodium pyrophosphate and starch was tested for detergency with the following results. In soft water this combination product showed a relative detergency of 106% and in hard water of 115%. Substantially no suds was produced during washing.

Example 2

100 g. of rosin, to which 0.5 g. of KOH was added, was treated to 150° C. to 160° C. and ethylene oxide gas passed in until 146 g. had been condensed with the rosin. Approximately 10 moles of ethylene oxide per mole of abietic acid had been combined, the detergency of this product was 114% in soft water and 65% in hard water. When combined with tetrasodium pyrophosphate and starch in the proportions utilized in Example 1 above, a dry, non-caking, difficultly flowing powder was obtained. This combination product had a relative detergency of 118% in soft water and 129% in hard water.

Example 3

100 g. of rosin containing 0.5 g. of KOH was heated to 150° C. to 160° C. Ethylene oxide was passed in until 218 g. had been absorbed by the rosin. The relative detergency of this product in soft water was 126% and in hard water 120%. Combined with tetrasodium pyrophosphate and starch in the proportions employed in Example 1, a dry, free-flowing powder was obtained which showed a detergency of 124% in soft water and 137% in hard water.

Example 4

100 g. of crude tall oil contained in a glass flask was heated in an oil bath to a temperature of about 130 C. and ethylene oxide in the gaseous form was passed into the tall oil until approximately 70 g. of ethylene oxide had combined. The condensation product so obtained was a dark, pleasant smelling, oily product which was partly soluble in water.

Employed per se as a detergent in 0.2% concentration it showed a relative detergency of zero in both soft and hard water, as measured by the standard Launderometer procedure.

A built product was now prepared containing 20% by weight of the tall oil-ethylene oxide product, prepared above, together with 40% of tetrasodium pyrophosphate and 40% of starch. This product was now tested by the same washing procedure as used above and found to have a relative detergency in soft water of 119% and in hard water of 127%. Very little suds was produced.

Example 5

100 g. of crude tall oil was treated as in Example 4 above with ethylene oxide until 85 g. of ethylene oxide had been combined with the tall oil. This product was then tested according to the standard Launderometer procedure and found to have a relative detergency in soft water of 30% and in hard water of 18%.

The above product was then mixed with tetrasodium pyrophosphate and starch in the proportions of 20% of the ethylene oxide-tall oil con-

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densation product, together with 80% of equal parts of tetrasodium pyrophosphate and starch and the built product then evaluated in the same manner as above. It was found that this material possessed a relative detergency of 120% in soft water and 145% in hard water. The detergent solution is substantially suds-free.

Example 6

In the same manner as described in Example 4 above, a condensation of ethylene oxide was carried out upon tall oil until 134 g. of ethylene oxide per 100 g. of tall oil had combined.

This product, when tested for detergency, showed a relative detergency of 90% in soft water and of 89% in hard water.

This product was then built as described in Example 5 and the built product found to have a relative detergency of 108% in soft water and 127% in hard water. The product washed without producing a suds.

Example 7

In the same manner as described in Example 4 above, a condensation of ethylene oxide with tall oil was carried out, the amount of ethylene oxide employed being 2.0 parts per part of tall oil. This product was tested for detergency by the standard method referred to above, and showed a relative detergency of 109% in soft water and a relative detergency of 131% in hard water.

Upon incorporating this material with a builder consisting of equal parts by weight of tetrasodium pyrophosphate and starch in such proportions as to produce a composition containing 20% of the condensation product, a determination of detergency resulted in a value of 111% in soft water and 129% in hard water. Substantially no suds is produced during washing.

The single figure of the drawing illustrates graphically the effect of the builder upon the detergency of the ethylene oxide-tall oil products. In the present figure the relative detergency of the products produced by reacting crude tall oil with amounts of ethylene oxide varying from 0.5 part of ethylene oxide per part of tall oil up to 2.0 parts of ethylene oxide per part of tall oil are graphically compared with and without a builder. In the figure, Curve A shows the relative detergency per se of the condensation products produced upon condensing the tall oil with from 0.5 part of ethylene oxide per part of tall oil (50 g. of ethylene oxide per 100 g. of tall oil) up to 2.0 parts of ethylene oxide per part of tall oil (200 g. of ethylene oxide per 100 g. of tall oil). Curve B shows the relative detergency of the same compositions when combined with a builder, the builder employed consisting of equal parts by weight of pearl starch and tetrasodium pyrophosphate, the detergent composition containing 20 parts of the ethylene oxide-tall oil condensation product and 80 parts of the builder.

The specific builder employed in the tests, the results of which are shown graphically in the figure, may, of course, be varied in composition and in content as is more fully described herein-after.

For producing the present detergent compositions the ethylene oxide condensation product is mixed with a sodium phosphate. Suitable phosphates are any of the polyphosphates such as the crystalline sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$; or sodium tetrakisphosphate, $\text{Na}_6\text{P}_4\text{O}_{13}$; or fused or sintered products approximating these compositions. Sodium hexa-metaphosphate, sodium py-

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rophosphate and particularly the tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, may be used, these products being preferred in the anhydrous form, although the hydrated form may also be used. Sodium orthophosphates, such as trisodium orthophosphate, may also be employed. When the hydrated form of the above salts are utilized, allowance should be made for the amount of water contained therein, in order to maintain the ingredients, when dissolved in water, within the range of proportions indicated.

An important ingredient of the present detergent compositions are the carbohydrate materials, starch and carboxymethylcellulose.

The starch used may be ordinary corn or potato starch and may be employed in the granular form known as "pearl" starch or it may be employed in the finely powdered form. Carboxymethylcellulose, which is an important additive, is described in the Journal of Industrial and Engineering Chemistry, 38, 942. It is available in various forms. The type which is soluble in alkalies and which is known as the "low substituted" type is preferred for compositions adjusted to an alkaline pH.

The detergent compositions should consist in parts by weight of from 15 to 30 parts of the ethylene oxide condensation product, above described, from 20 to 50 parts, anhydrous basis, of a phosphate salt selected from the class consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium orthophosphate and sodium hexametaphosphate and mixtures thereof, and the balance to make 100 parts of a carbohydrate material selected from the class consisting of starch and carboxymethylcellulose and mixtures of said starch and carboxymethylcellulose. When mixtures of the stated carbohydrate materials are employed, it is preferred to use from 0.1% to 5% by weight of carboxymethylcellulose based on the composition.

The present application is a continuation-in-part of our application Serial No. 637,096, filed December 22, 1945 now abandoned.

What we claim is:

1. A detergent composition consisting in parts by weight of from 15 to 30 parts of the condensation product of abietic acid with ethylene oxide, said condensation product containing at least 0.5, but less than 2.3, parts of condensed ethylene oxide per part of abietic acid, from 20 to 50 parts, anhydrous basis, of a phosphate salt selected from the group consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium phosphate and sodium hexametaphosphate and mixtures thereof, and the balance to make 100 parts of a carbohydrate material selected from the group consisting of starch and carboxymethylcellulose and mixtures thereof.

2. A detergent composition consisting in parts by weight of from 15 to 30 parts of the condensation product of tall oil with ethylene oxide, said condensation product containing at least 0.5 part, but less than 2.3 parts, of condensed ethylene oxide per part of tall oil, from 20 to 50 parts, anhydrous basis, of a phosphate salt selected from the group consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium phosphate and sodium hexametaphosphate and mixtures thereof and the balance to make 100 parts of a carbohydrate material selected from the group consisting of starch and carboxymethylcellulose and mixtures thereof.

3. A detergent composition consisting in parts by weight of from 15 to 30 parts of a condensa-

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tion product of rosin with ethylene oxide, said condensation product containing at least 0.5 part, but less than 2.3 parts, of condensed ethylene oxide per part of rosin, from 20 to 50 parts, anhydrous basis, of a phosphate salt selected from the group consisting of tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium phosphate and sodium hexametaphosphate and mixtures thereof and the balance to make 100 parts of a carbohydrate material selected from the group consisting of starch and carboxymethylcellulose and mixtures thereof.

4. A detergent composition consisting in parts by weight of from 15 to 30 parts of the condensation product of tall oil with ethylene oxide, said condensation product containing at least 0.5 part, but less than 2.3 parts, of condensed ethylene oxide per part of tall oil, from 20 to 50 parts, anhydrous basis, of tetrasodium pyrophosphate and the balance to make 100 parts of a carbohydrate material selected from the group consisting of starch and carboxymethylcellulose.

5. A detergent composition consisting in parts by weight of from 15 to 30 parts of a condensa-

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tion product of tall oil with ethylene oxide, said condensation product containing at least 0.5 part, but less than 2.3 parts of condensed ethylene oxide per part of tall oil, from 20 to 50 parts, anhydrous basis, of sodium tripolyphosphate, and the balance to make 100 parts of a carbohydrate material selected from the group consisting of starch and carboxymethylcellulose.

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The following references are of record in the file of this patent:

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