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Patented Oct. 13, 1942

2,298,650

spray drying

UNITED STATES PATENT OFFICE

2,298,650

PARTICULATE DETERGENT COMPOSITION

Nicholas N. T. Samaras and Jay C. Harris,
Dayton, Ohio, assignors to Monsanto Chemical
Company, St. Louis, Mo., a corporation of Dela-
ware

XRS: *none*

No Drawing. Application May 23, 1940,
No. 336,716

10 Claims. (CL 252-161) *252-559*

The present invention relates to new particulate detergent compositions which are free-flowing and substantially non-hygroscopic and non-caking.

Many of the commercial preparations of detergent compositions, and in particular detergent compositions comprising water-soluble salts of alkylated aromatic sulfonic acids, exhibit the undesirable property of wetting down on exposure to the atmosphere. Such caking or wetting down of the detergent composition is of such inconvenience and undesirability as to substantially preclude their commercial use. The improved particulate detergent compositions of the present invention are not substantially affected by atmospheric moisture and as a result retain their particulate form when subjected to conditions which produce melting and caking of other particulate detergent compositions.

The present application is a continuation-in-part of our co-pending application Serial No. 183,509, filed January 5, 1938.

The principal object of the present invention is to provide a detergent composition in particulate form which shall be characterized by especially high detergent efficiency and which shall dissolve rapidly in water, be substantially unaffected by atmospheric moisture conditions normally prevailing in different geographical localities, and which shall be substantially free of fine particles that are readily borne by circulating air currents in the home and substantially free from any tendency to disintegrate into finer particles on standing or shaking. The detergent composition shall be of stable particulate form, have a low apparent specific gravity and be free from fine dust particles and shall be stable and free from caking tendency under prevailing atmospheric conditions.

In accordance with the present invention it has been discovered that a detergent composition conforming in a remarkable degree to the specifications outlined in the foregoing object can be made by spray-drying an aqueous solution or a uniform or homogeneous suspension comprising sodium sulfate and certain alkylated aromatic hydrocarbon sulfonic acid salts which are specified hereinafter. By observing certain ratios of constituents and conducting the drying in such a manner as to leave a determinate moisture content in the product, free-flowing relatively non-hygroscopic particulate detergent compositions having an apparent specific gravity within the range of 0.05 to 0.25 are obtained.

The ratio of sodium sulfate to the salt of the

alkylated aromatic hydrocarbon sulfonic acid may be varied widely provided at least approximately 20% sodium sulfate is present, but compositions having optimum non-caking characteristics and detergent efficiency and which are at the same time of low apparent specific gravity and free from tendency to disintegrate are those comprising 20% to 80% sodium sulfate and preferably 35% to 65%, while the content of alkylated aromatic sulfonic acid salt is 80% to 20% and preferably 65% to 35%. Small proportions of additional detergent builders such as magnesium sulfate may be present without changing the properties of the composition substantially. Sodium sulfate may be replaced by sodium carbonate in such compositions up to about 50% or more of the detergent builder content (see, for example Detergent Mix B hereinafter) with but slight changes in general characteristics but with significant changes in the alkalinity of the detergent composition, that is, a detergent of this class containing sodium carbonate is slightly alkaline but one containing only sodium sulfate as the constituent other than the alkylated aromatic hydrocarbon sulfonic acid salt is approximately neutral in reaction. Similarly, some of the sodium sulfate may be replaced by builders such as tetrasodium pyrophosphate, borax and the like.

In the preparation of the detergent composition, the composition should not be dried to the total exclusion of moisture. The particulate solid composition should have a moisture content of from approximately 1.0% to 5.0% water. By observing these limits undesirable fragmentation or disintegration into fine powder is inhibited and the tendency to produce dust or undesirable fines on standing or shaking is eliminated. Compositions which have been dried to the exclusion of all moisture have a tendency to absorb moisture, which absorption may be accompanied by disintegration of the original particles. Greater proportions of combined moisture when present in the product may produce liberation of moisture from the product under atmospheric conditions prevailing in certain localities, as a result of which disintegration and dusting of the particles together with localized caking of the entire bulk is likely to occur.

The invention involves the discovery not only that certain specific proportions of sodium sulfate and the alkylated aromatic hydrocarbon sulfonic acid salt must be observed to obtain a particulate product which on spray-drying will be substantially stable, free-flowing and non-caking,

but that the moisture content of the final product must also be controlled since the combined moisture has a binding or cohesive effect on the individual particles and prevents absorption or liberation of substantial proportions of moisture which are accompanied by disintegration or crumbling of the particles. The low apparent specific gravity of the product is also of importance since the particles are "blown up" or hollow and this indirectly is connected with the tendency of the particles to absorb and liberate water without wetting down and caking and without disintegration or crumbling of the individual particles. Particulate detergents of this type having a lower apparent specific gravity than 0.05 are unstable, friable, and disintegrate on standing into finer particles and dust. Particulate detergents such that substantially all particles are retained on an 80-mesh sieve are preferred.

The salts of alkylated aromatic hydrocarbon sulfonic acids which are contemplated for use in this invention are water-soluble, particularly alkali-metal, salts of alkylated benzene sulfonic acids in which at least one alkyl group contains from 11 to 15 carbon atoms and mixtures thereof. Sodium salts of alkylated benzene sulfonic acids are preferred. Such salts of alkylated aromatic hydrocarbon sulfonic acids and methods for their preparation are described in Kyrides' Patent No. 2,161,174 and in our co-pending application referred to hereinabove. Alkali-metal salts of sulfonic acids of undecyl, dodecyl, tridecyl, tetradecyl and pentadecyl substituted benzene, toluene, xylene and similar aromatic hydrocarbons of the benzene series, as well as their isomers and mixtures thereof, are included within the ambit of the invention.

Heretofore, in the manufacture of detergent compositions from water-soluble, metallic salts of alkylated aromatic sulfonic acids in which the alkyl group contains more than 8 and less than 16 carbon atoms, great difficulty and inconvenience in handling were experienced because of the tendency of the materials to cake and deliquesce. Attempts to remedy or eliminate this undesirable property of the products by the simple mechanical admixture of anhydrous sodium sulfate with the water-soluble alkali-metal salts of said alkylated aromatic sulfonic acids did not result in a free-flowing, non-hygroscopic solid. Similarly, on grinding dodecyl benzene sodium sulfonate with an equal weight of a mixture of equal parts by weight of sodium chloride and sodium benzene monosulfonate, the powdered product caked to a semi-solid after less than six days of exposure to 60% relative humidity. However, on spray-drying aqueous solutions or homogeneous suspensions of the alkylated aromatic sulfonate containing sodium sulfate, according to the present invention, the caking and deliquescing of the detergent is unexpectedly eliminated and the product possesses the other desirable properties referred to herein.

A great variety of detergent compositions have been made with a mixture of dodecyl and tridecyl benzene sodium sulfonates and an equal part by weight of sodium sulfate or other salt in efforts to produce a free-flowing non-caking and non-crumbling particulate detergent composition. These compositions were made by spraying aqueous solutions or suspensions of the desired composition into a heated chamber, according to the method of the present invention. The dried particulate compositions were then

exposed for varied periods to atmospheres having a relative humidity of 60% or more. The composition made with sodium sulfate in this manner retained its particulate form, was free-flowing, and was dry in appearance after six days. Compositions made with tetrasodium pyrophosphate, borax and sodium silicate, respectively, in place of the sodium sulfate, were caked at the end of six days, the silicate mixture being a solid mass. The percentages of moisture absorbed in the last three cases were not substantially different, although it was higher in all cases than that of the composition containing sodium sulfate, yet the degree and character of the caking was different and was most marked in the case of sodium silicate. The problem is obviously not solely one of moisture absorption alone. Furthermore, a great variety of salts which might otherwise appear useful for the purpose of preventing caking of the detergent compositions could not be used because of their adverse effect on the detergent characteristics of the composition. In this respect sodium sulfate is unique in that it enhances the detergent activity of the composition and has a most desirable effect on the physical characteristics of the resulting spray-dried product.

It is believed that under the conditions of drying specified in the present invention the sodium sulfate is present in the product in a form analogous to the beta form of anhydrous sodium sulfate and that in the product the alkali-metal salt of the alkylated aromatic hydrocarbon sulfonic acid prevents transformation of the beta form to the alpha form. It is known (see J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," London, Longmans, Green Co., vol. II, 1927, page 661) that the beta form of anhydrous sodium sulfate does not hydrate while the alpha form combines immediately with water at 25° and that hydration of the beta form starts only when it has passed into the alpha form.

Any suitable apparatus and method of spray-drying aqueous solutions or suspensions of the alkylated benzene sulfonate and sodium sulfate may be used provided the process is adjusted to obtain a particulate product having an apparent specific gravity within the range of 0.05 to 0.25 and a moisture content of 1.0% to 5.0% and a desired uniform particle size (80 mesh screen or thereabout). Methods and apparatus for spray-drying are described in the articles by W. S. Bowen in Ind. Eng. Chem., 1938, vol. 30, page 1001-2 and Ben B. Fogler and Robert W. Kleinschmidt, Ind. Eng. Chem., 1938, vol. 30, pages 1372-84. Preferably the system is adjusted so that a powder the individual particles of which are of such size that the powder is almost completely retained on an 80-mesh sieve is obtained.

The invention is not limited to any specific method of spray-drying whereby a product of this character is obtained. However, a spray-drying unit of conventional type consisting of a chamber provided with a hopper at the bottom, an inlet for heated gases, and an outlet for exhaust gases, an inlet for feeding heated solutions or suspensions of the composition to be dried, and a disc spray wheel driven by a variable speed electric motor and capable of rotating at a speed of 6000 R. P. M. or greater has been used for this purpose. Subdivision of the solution or suspension is effected on the spray wheel itself and by the centrifugal force

of the wheel when in motion. The drying chamber or tower into which the subdivided solution or suspension is passed is heated by means of hot air introduced by suitable means at the top of the tower and circulated from the top to the bottom thereof, from which point the cooled air passes through an outlet together with any finely divided solids into additional towers and finally through water sprays to remove all solids remaining in the exit gases. If convenient or desirable, cold air may be introduced preferably at the bottom of the tower to reduce the temperature of both the exit gases and the condensed solid.

By means of this type of equipment products conforming to the hereinabove described characteristics were obtained. Variations in characteristics within these limits can be obtained by changes in the temperature, concentration and rate of feed of the solution or suspension to be dried, speed of the rotating spray disc, and temperature and volume of the inlet gases. A degree of control of the entire unit can be maintained by observation of the temperature of the outlet gases. When such a unit is operating to produce a determinate character of product, any changes in the temperature of the exit gases is an indication that some other part of the system is not operating properly, hence checking should be instituted and compensation should be made therefor by changing the temperature of the feed solution or suspension or the feed rate, by changing the volume or temperature of the inlet gases or by admitting cooler air, or by speeding up or slowing down the disc sprayer although this latter factor is more directly connected with the size and character of the particles than with their dryness.

It is important that the sodium sulfate and alkali-metal salt of the alkylated aromatic hydrocarbon sulfonic acid be present in solution before drying or be in the form of a homogenous uniform suspension or slurry; otherwise products which cake in masses throughout the batch are likely to result.

The following examples are illustrative of the invention and represent the results of operating in such a spray-drying unit under different operating conditions and the character of the products obtained. In these examples the solid detergent components of the feed stocks which were used were present in the following proportions in parts by weight:

Detergent Mix A

	Parts
Mixture of dedecyl and tridecyl benzene sodium sulfonates	100
Sodium sulfate (anhydrous basis)	100
Magnesium sulfate (anhydrous Mg SO ₄ basis)	2

Detergent Mix B

Mixture of dodecyl and tridecyl benzene sodium sulfonates	100
Sodium sulfate (anhydrous basis)	60
Sodium carbonate (anhydrous basis)	40
Magnesium sulfate (anhydrous Mg SO ₄ basis)	2

Detergent Mix C

Sodium alkyl benzene sulfonate consisting of a mixture of compounds derived from alkylation of benzene by a kerosene boling within the range 190° to 230° C.	40
Sodium sulfate (anhydrous basis)	60

EXAMPLE I

Operating conditions

Feed stock	40% suspension of Detergent Mix A in water.
Temperature of feed stock	54° C.
Inlet gas temperature	232° C.
Outlet gas temperature	121° C.
Spray wheel type	Small labyrinth type.
Speed of spray wheel	3000 R. P. M.

Product

Apparent specific gravity	0.1330
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Sieve test:

	Per cent
On 30 mesh	22.0
On 40 mesh	39.4
On 60 mesh	30.6
On 80 mesh	4.8
On 100 mesh	2.5
Through 100 mesh	0.7

EXAMPLE II

Operating conditions

Feed stock	50% suspension of Detergent Mix B.
Temperature of feed stock	60° C.
Inlet gas temperature	232° C.
Outlet gas temperature	143° C.
Spray wheel type	Non-shearing type.
Speed of spray wheel	3000 R. P. M.

Product

Apparent specific gravity	0.1287
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Six-day relative humidity tests:

Relative humidity	60% 85% 93%
Per cent moisture absorbed	None 2.3 2.6

Sieve test:

	Per cent
On 30 mesh	5.2
On 40 mesh	30.3
On 60 mesh	32.7
On 100 mesh	24.4
Through 100 mesh	6.6

EXAMPLE III

Operating conditions

Feed stock	50% suspension of Detergent Mix A in water.
Temperature of feed stock	60° C.
Inlet gas temperature	232° C.
Outlet gas temperature	121° C.
Spray wheel type	Small labyrinth type.
Speed of spray wheel	3000 R. P. M.

Product

Apparent specific gravity	0.0976
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Sieve test:

	Per cent
On 30 mesh	58.7
On 40 mesh	23.6
On 60 mesh	14.6
On 80 mesh	2.2
On 100 mesh	0.7
Through 100 mesh	0.2

EXAMPLE IV

Operating conditions

Feed stock----- 40% suspension of
Detergent Mix C. 5
Temperature of feed stock.. 90° C.
Inlet gas temperature----- 260° C.
Outlet gas temperature----- 160° C.
Spray wheel type----- Small labyrinth type.
Speed of spray wheel----- 6000 R. P. M. 10

Product

Apparent specific gravity----- 0.0785
Sieve test:

	Per cent 15
On 20 mesh-----	8.7
On 40 mesh-----	58.9
On 60 mesh-----	27.1
On 80 mesh-----	3.3
Through 80 mesh-----	2.0 20

The products of the foregoing examples were all free-flowing, dry powders which retained their free-flowing character after exposure for six days to atmospheres having humidities of 60%, 85% and 93%. The percentage moisture absorbed in such humidity tests are exemplified in the results reported for the products of Example 2. The test is performed as follows: Definite weighed portions of the detergent under test were placed in open containers which in turn were placed in jars containing saturated aqueous solutions of appropriate inorganic salts in contact with an excess of the solid phase chosen so as to produce 60%, 85% and 93% relative humidities. The jars containing the detergent were then tightly closed and allowed to stand for six days, at the end of which time they were opened and the condition of the detergent noted as to increase in weight and whether or not it had caked or remained free-flowing. The character of the product is of greater significance than the percentage moisture absorbed since other materials which have absorbed the same amount of moisture may be entirely wetted and caked.

The sieve test used is similar to that of the A. S. T. M. and represents the relative content and varying size of the different particles of the composition. For comparison with the tests of the foregoing examples, the screen tests of several commercial detergent compositions obtained in the market were as follows:

	"Vel"	"Dreft"	"Super Suds"	"Super Suds Concentrated"
	Per cent	Per cent	Per cent	Per cent
On 40 mesh-----	0.8	72.4	70.8	67.1
On 60 mesh-----	17.6	15.1	19.7	22.7
On 100 mesh-----	54.4	7.8	7.5	7.8
On 150 mesh-----	14.0	3.1	1.2	1.6
On 200 mesh-----	4.8	0.8	0.4	0.4
Through 200 mesh-----	4.8	0.8	0.4	0.4
Loss-----	3.6			

Particles having a size smaller than 100 mesh are a fine dust and are easily blown about by air currents in the home.

The apparent specific gravity referred to hereinabove and as used throughout this specification was determined in the following manner: Twenty-five grams of the dried detergent mixture was placed in a 250 cc. graduated cylinder, after which the cylinder and contents were dropped 50 times from a height of 3 inches and the volume of the compacted detergent mixture noted at a temperature of 30° C. Twenty-five

grams of water occupies a volume of 25.1 cc. at 30° C. The volume of 25 grams of water at 30° C. divided by the volume of the same weight of the detergent powder at 30° C. gives the apparent specific gravity of the detergent powder.

Preferably the compositions for use according to this invention are such as contain 40% active alkylated aromatic hydrocarbon sulfonate. Such compositions are, for example, represented by Detergent Mix C or by the following compositions, which can be spray-dried according to the method disclosed herein. All proportions stated are in parts by weight of anhydrous materials.

EXAMPLE V

	Parts
Sodium sulfate-----	36
Sodium carbonate-----	24
Alkylated aromatic hydrocarbon sulfonate--	40
Magnesium sulfate-----	2

EXAMPLE VI

	Parts
Dodecyl benzene sodium sulfonate-----	40
Sodium sulfate-----	58.5
Magnesium sulfate-----	0.5
Diethylene glycol-----	0.5

EXAMPLE VII

	Parts
Dodecyl benzene sodium sulfonate-----	40
Sodium sulfate-----	38.5
Sodium carbonate-----	20
Magnesium sulfate-----	0.5
Diethylene glycol-----	0.5

The diethylene glycol which is present in the compositions of Examples VI and VII is used to prevent dusting of any fine particles originally formed as a result of imperfect control of particle size in the spray-drying operation. It may be replaced by glycerol or similar material to be entirely omitted.

Examples VI and VII which contain a smaller added proportion of magnesium sulfate than other disclosed products are particularly suitable for preparations made by dissolving or homogeneously suspending the materials in water containing some original hardness. The hardness of the water, representing magnesium and other metal salts, will be found in the final spray-dried product. When the water used for this purpose is soft or distilled water a greater proportion of magnesium sulfate will be required to compensate for the magnesium salts that are absent from the water. Generally from about 0.5 to 1.0% magnesium sulfate (anhydrous basis) is desired in the final spray-dried product.

By operating according to the present invention a substantially uniform non-caking, free-flowing, particulate detergent composition can be obtained, which is not the case when the water-soluble salt of the aromatic hydrocarbon sulfonic acid is dried in a mass and mechanically mixed with sodium sulfate or when a solution of the aromatic hydrocarbon sulfonic acid salt and sodium sulfate in indiscriminate proportions is dried in a mass and then disintegrated mechanically by grinding. Uniformity of particle size cannot be controlled mechanically nor can the caking characteristics be controlled by purely empirical methods, as is evident from the foregoing description.

It is to be understood that the invention is not to be limited by the specific examples hereinabove set forth as they are to be understood as illustrative only. The invention is limited solely by the following claims.

We claim:

1. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise a mixture of 35 to 65 parts by weight of sodium sulfate and 65 to 35 parts by weight of a water-soluble salt of a monoalkyl-substituted aromatic hydrocarbon sulfonic acid selected from the group consisting of water-soluble salts of monoalkyl-substituted benzene, toluene and xylene sulfonic acids, the substituted alkyl groups of which contain at least 11 and less than 16 carbon atoms, to each 100 parts by weight of the solid constituents.

2. A non-caking, free-flowing particulate solid detergent composition of which substantially all the individual particles thereof are retained on an 80-mesh sieve and which has an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise a mixture of 35 to 65 parts by weight of sodium sulfate and 65 to 35 parts by weight of an alkali-metal salt of a monoalkyl-substituted aromatic hydrocarbon sulfonic acid selected from the group consisting of alkali-metal salts of monoalkyl-substituted benzene, toluene and xylene sulfonic acids, the substituted alkyl groups of which contain at least 11 and less than 16 carbon atoms, to each 100 parts by weight of the solid constituents.

3. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise a mixture of 35 to 65 parts by weight of sodium sulfate and 65 to 35 parts by weight of an alkali-metal salt of a monoalkylated benzene sulfonic acid, the alkyl group of which contains at least 11 and less than 16 carbon atoms, to each 100 parts by weight of the solid constituents.

4. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise a mixture of 35 to 65 parts by weight of sodium sulfate and 65 to 35 parts by weight of a sodium salt of a monoalkylated benzene sulfonic acid, the alkyl group of which contains at least 11 and less than 16 carbon atoms, to each 100 parts by weight of the solid constituents.

5. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise a mixture of 35 to 65 parts by weight of sodium sulfate and 65 to 35 parts by weight of sodium salts of a mixture of mono-

alkylated benzene sulfonic acids, the alkyl groups of which contain at least 11 and less than 16 carbon atoms, to each 100 parts by weight of the solid constituents.

6. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise the following substances in approximately the following proportions by weight: 60 parts of sodium sulfate and 40 parts of sodium salts of a mixture of monoalkylated benzene sulfonic acids, the alkyl groups of which contain at least 11 and less than 16 carbon atoms, to each 100 parts of the solid constituents.

7. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise the following substances in approximately the following proportions by weight: 36 parts of sodium sulfate, 24 parts of sodium carbonate and 40 parts of sodium salts of a mixture of monoalkylated benzene sulfonic acids, the alkyl groups of which contain at least 11 and less than 16 carbon atoms, to each 100 parts of the solid constituents.

8. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise the following substances in approximately the following proportions by weight: 58.5 parts of sodium sulfate, 40 parts of dodecylbenzene sodium sulfonate and 0.5 part of magnesium sulfate (anhydrous basis), to each 99 parts of the solid constituents.

9. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise the following substances in approximately the following proportions by weight: 58.5 parts of sodium sulfate, 40 parts of dodecylbenzene sodium sulfonate and 0.5 part of diethylene glycol, to each 99 parts of the solid constituents.

10. A non-caking, free-flowing particulate solid detergent composition having an apparent specific gravity of about 0.05 to 0.25 and a moisture content of about 1.0 to 5.0% obtained by spray-drying an aqueous solution or homogeneous aqueous suspension, the solid constituents of which comprise the following substances in approximately the following proportions by weight: 58.5 parts of sodium sulfate, 40 parts of dodecylbenzene sodium sulfonate, 0.5 part of magnesium sulfate (anhydrous basis) and 0.5 part of diethylene glycol, to each 99.5 parts of the solid constituents.

NICHOLAS N. T. SAMARAS.
JAY C. HARRIS.

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CERTIFICATE OF CORRECTION.

Patent No. 2,298,650.

October 13, 1942.

NICHOLAS N. T. SAMARAS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 42, for "homogenous" read --homogeneous--; line 56, for "dodecyl" read --dodecyl--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of November, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.