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2,963,438

STABILIZED SOAP COMPOSITION

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No Drawing. Filed Apr. 14, 1955, Ser. No. 501,437

15 Claims. (Cl. 252—107)

This invention relates to improved compositions containing fatty acid radicals. More particularly, it relates to soap compositions stabilized with respect to color and odor formation by the incorporation therein of hydrazides. In a more particular aspect, this invention relates to the stabilization of soap compositions containing phenolic bactericides by the incorporation therein of hydrazides.

The tendency of soaps to discolor and become rancid in storage or use is well known. These effects have been attributed to a variety of causes including the manufacture of soaps from fats and oils which themselves tend to become rancid. It is also believed that minor metallic contaminants particularly iron and copper in minute amounts accelerate the formation of oxidation products resulting in undesirable odor or discoloration. These effects may appear in various forms of soap including bar soap, powdered soap, granulated soap and spray-dried soaps in the form of beads.

The principal method of attack of this problem has been to add various anti-oxidants or other stabilizers to soap compositions in an effort to overcome these effects. Many of these suggested inhibitors afford a partial solution, for example, in inhibiting odor formation without affecting or even deleteriously affecting color stability.

Soaps in liquid form, usually potassium soaps, are more difficult to stabilize in these respects than sodium soaps and many of the proposed stabilizers are generally unsatisfactory for the production of stable potassium soaps or blends containing substantial amounts of potassium soaps.

The problem of soap stabilization has more recently been further aggravated by the incorporation of phenolic bactericides in soap. Although phenolic anti-oxidants have been proposed for the stabilization of soap, many are ineffective and some phenolic compounds even accelerate the deterioration. A commonly used phenolic bactericide in soap is 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenylmethane (hexachlorophene). Small proportions, for example, 0.5 percent in soap appear to accelerate color formation. This effect may be masked by the incorporation of yellow coloring matter in the composition so that subsequent yellowing during storage or use is not so obvious. The problem of incorporation of such phenolic bactericides in white toilet soap so far has not been solved. It is important therefore to provide new and improved stabilizers for soap which are effective in the presence of phenolic bactericides.

It has now been discovered that soap compositions can be stabilized by the incorporation therein of minor proportions of hydrazides. It has further been discovered that these stabilizers are particularly effective in soap compositions containing phenolic bactericides. Useful pro-

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portions of the hydrazides vary from a minimum effective amount, suitably about 0.05 percent to about 1 percent by weight, based on the weight of the soap.

Suitable hydrazides which can be used in accordance with the present invention include the monohydrazides of aliphatic monocarboxylic acids containing from 1 to 18 carbon atoms, such as formic acid hydrazide, acetic acid hydrazide, propionic acid hydrazide, butyric acid hydrazide, valeric acid hydrazide, caproic acid hydrazide, lauric acid hydrazide, myristic acid hydrazide, palmitic acid hydrazide, stearic acid hydrazide and elaidic acid hydrazide. The hydrazides of dibasic acids, such as those derived from oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, sebacic acid and fumaric acid can also be utilized. Also useful are the hydrazides of monobasic aromatic acids, such as benzoic acid hydrazide, o-nitrobenzoic acid hydrazide, p-nitrobenzoic acid hydrazide, o-toluic acid hydrazide, p-toluic acid hydrazide, m-toluic acid hydrazide, salicylic acid hydrazide, 1-naphthoic acid hydrazide and 2-naphthoic acid hydrazide. The dihydrazide of carbonic acid, carbodihydrazide, is also very effective. Hydrazides derived from substituted hydrazines can be used, for example, the beta-hydroxyethylhydrazide of stearic acid, the di-(beta-hydroxyethyl) hydrazide of stearic acid, the unsymmetrical dimethylhydrazide of oleic acid and the phenylhydrazide of kerylbenzene sulfonic acid. Mixtures of hydrazides of organic acids, hydrazides of mixed fatty acids and mixtures of hydrazides with known compatible soap stabilizers can be used.

The stabilizers should not be added to the soap compositions at a stage which will result in decomposition, leaching, or deterioration of the stabilizing agent. They can be incorporated in the soap compositions at any convenient step after the saponification. For example, they can be added to the neat soap as made in the kettle in the manufacture of frame soap. In the manufacture of milled soap, it is ordinarily preferable to add the stabilizer to the mixer preceding the milling together with perfume materials and coloring agents if desired. The stabilizer can also be incorporated during the crutching process. The stabilizers can be added conveniently in the form of aqueous solutions where the stabilizers are water soluble or they can be incorporated as dry solids, preferably finely divided. Mixing subsequent to the addition of the stabilizer should be sufficient to render the soap composition homogeneous.

The soap product can subsequently be dried and formed into cakes, plates, beads or other forms as desired. In the manufacture of liquid soap compositions the stabilizers can be dissolved in the soap solutions or aqueous solutions of the stabilizers when conveniently prepared can be added to the liquid soap composition.

The stabilizers are effective in soaps subsequently incorporated in cosmetic compositions including tooth paste, face creams and body creams.

Example 1

Blends of soap with acetic hydrazide and sebacic dihydrazide were prepared by thoroughly mixing 0.5 part by weight of the hydrazide with 99.5 parts by weight of dried pure soap stock (essentially the sodium salt of tallow fatty acids) at room temperature. The mixture was pressed into 20 gram bars under a pressure of 2000 p.s.i.g. Four test bars of each hydrazide blend and four similar bars prepared from the same soap stock omitting the hydrazide were stored in an oven at 110° C.

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for 7 days. At the end of this period, the light reflected from the surface of the blocks was measured with a Hunter reflectometer. Taking the reflectance of the soap immediately after preparation as 100 percent, the following average results were obtained:

Stabilizer, percent	Treatment	Light Reflectance, percent
None.....	Unheated.....	100.0
Do.....	Heated.....	55.5
Acetic hydrazide, 0.5 weight percent.....	do.....	64.3
Sebacic dihydrazide, 0.5 weight percent.....	do.....	75.1

The data show extensive color development in the untreated soap caused by the accelerated test. Significant inhibition of color development is shown by the addition of either acetic hydrazide or sebacic dihydrazide.

Example II

Acetic hydrazide and carbohydrazide were tested as stabilizers by the test described in Example I. The following results were obtained:

Stabilizer, percent	Treatment	Light Reflectance, percent
None.....	Unheated.....	100.0
Do.....	Heated.....	30.5
Acetic hydrazide, 0.05 weight percent.....	do.....	43.5
Carbohydrazide, 0.5 weight percent.....	do.....	49.5

Even at a concentration of 0.05 weight percent, acetic hydrazide showed significant improvement in preventing color formation. Carbohydrazide at 0.5 weight percent was also very effective.

Example III

White soap flakes (essentially the sodium soap of tallow fatty acids) were used as the soap stock in further tests according to the procedure of Example I. The following reflectances were obtained:

Stabilizer, percent	Treatment	Light Reflectance, percent
None.....	Unheated.....	100.0
Do.....	Heated.....	23.5
Lauric hydrazide, 0.05 weight percent.....	do.....	34.4

Lauric hydrazide at a concentration of 0.05 weight percent showed a significant stabilization of the soap with respect to color development.

Example IV

A liquid potassium coconut oil soap was prepared by heating a mixture of 420 grams of coconut oil, 300 grams of 36 percent aqueous potassium hydroxide and 1867 grams of water on a steam bath for 16 hours. Sufficient 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenylmethane, also known as hexachlorophene, was dissolved in the solution so that it contained 0.5 weight percent of the hexachlorophene, based on the dry weight of the soap. To a 50 milliliter portion of the soap solution containing hexachlorophene was added 0.26 gram of stearic hydrazide. The same amount of myristic hydrazide was added to another 50 milliliter portion of the soap solution. The two test samples together with a 50 milliliter test sample containing hexachlorophene and another without hexachlorophene were heated in an oven at 100-120° C. for two weeks. Most of the water evaporated from the samples after a few hours of heating. At the end of the heating period, the samples were cooled to 28° C. and diluted to 50 milliliters with water. Any insoluble matter was removed by filtration and the light transmission of the filtrate was determined using

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a No. 525 series blue filter in a Fischer electrophotometer. The results shown in the following table were obtained:

Stabilizer	Hexachlorophene, percent	Treatment	Light Transmission, percent
None.....	None	Unheated.....	100.0
Do.....	None	Heated.....	60.0
Do.....	0.5	do.....	44.0
Stearic hydrazide.....	0.5	do.....	52.0
Myristic hydrazide.....	0.5	do.....	54.0

The data show that the hexachlorophene adversely affects the color stability of the soap solution and that the two hydrazides materially improve the stability in this respect.

Example V

Additional quantities of the same potassium soap solution as used in the preceding example were used in the following tests. Several hydrazides and commercial stabilizers were dissolved in separate 50 milliliter portions of the soap solution already containing 0.5 weight percent of hexachlorophene, based on dry soap weight, to make solutions containing 0.5 weight percent of the stabilizer, also based on dry soap weight. A portion of each solution was sealed in a glass ampule and heated in an oven at 80° C. for two weeks. At the end of this time, the ampules were cooled, opened and the percent light transmission based on that of the original unheated solution as 100 percent was measured with a Fischer electrophotometer using a No. 525 Series blue filter. The results shown in the following table were obtained:

Stabilizer, 0.5 percent	Hexachlorophene, percent	Treatment	Light Transmission, percent
None.....	None	Unheated.....	100.0
Do.....	0.5	Heated.....	87.5
Lauric hydrazide.....	0.5	do.....	90.0
Myristic hydrazide.....	0.5	do.....	100.0
Sebacic dihydrazide.....	0.5	do.....	97.5
Commercial Stabilizer No. 1.....	0.5	do.....	80.5
Commercial Stabilizer No. 2.....	0.5	do.....	61.0

The test is less severe than that of Example IV since the unstabilized soap after the test had a light transmission of 87.5 percent of the original. The hydrazides tested, however, showed material stabilization against the development of color. This is in contrast to the two commercial stabilizers which even appear to have an accelerating effect.

Various modifications can be made in the procedures of the specific examples to provide other improved soap and soap-containing compositions falling within the scope of our invention. Our invention is generally applicable for the purpose of improving the properties of soaps and soap-containing compositions as those terms are generally understood in the art. In the specific examples, the soaps employed were sodium soaps of tallow fatty acids or a potassium soap of coconut oil fatty acids. Other soaps can be substituted for those specifically used, and our invention comprehends the improvement of soaps and compositions containing them in which the cationic portion is, for example, ammonia, an amine, an alkali metal or an alkaline earth metal, such as sodium, potassium, lithium, calcium, barium, and so forth, as well as magnesium, aluminum, zinc and cadmium. The anionic portion of the soap is generally derived from one or more aliphatic monocarboxylic acids containing from 12 to 18 carbon atoms, such as lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and so forth. The soaps suitable for use in our invention can also be derived in known manner from a wide variety of naturally-occurring materials or derivatives thereof, including tallow, palm oil, hydrogenated marine oils such as whale oil, coconut oil, palm kernel oil, rosin, tall oil.

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lard, olive oil, cottonseed oil, peanut oil, soya bean oil, linseed oil, and so forth. Also, various other phenolic bactericides can be substituted for the hexachlorophenes used in the examples, among them being hexylresorcinol, cresol, thymol, chlorothymol and guaiacol.

Hydrazides may also be incorporated in greases. These are commonly soap-thickened petroleum oils containing lithium, sodium, calcium, aluminum or other metal soaps of various acids including those derived from tall oil, tallow, castor oil or waste fat acids, for example.

We claim:

1. A soap composition consisting essentially of an alkali metal soap of an aliphatic monocarboxylic acid containing from 12 to 18 carbon atoms and as a stabilizer a hydrazide selected from the group consisting of acetic acid hydrazide, sebacic acid dihydrazide, carbonyldihydrazide, lauric acid hydrazide, myristic acid hydrazide and stearic acid hydrazide in amount from 0.05 to 1 percent by weight, based upon the weight of the soap.

2. A composition according to claim 1 in which the soap is a sodium soap.

3. A composition according to claim 1 in which the soap is a potassium soap.

4. A composition according to claim 1 also containing an amount of a phenolic bactericide sufficient to impart bactericidal action to the soap.

5. A composition according to claim 1 in which the hydrazide is acetic acid hydrazide.

6. A composition according to claim 1 in which the hydrazide is sebacic acid dihydrazide.

7. A composition according to claim 1 in which the hydrazide is carbonyldihydrazide.

8. A composition according to claim 1 in which the hydrazide is lauric acid hydrazide.

9. A composition according to claim 1 in which the hydrazide is stearic acid hydrazide.

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10. A composition according to claim 1 in which the soap is a sodium soap and in which the hydrazide is acetic acid hydrazide.

11. A composition according to claim 1 in which the soap is a sodium soap and in which the hydrazide is sebacic acid dihydrazide.

12. A composition according to claim 1 in which the soap is a sodium soap and in which the hydrazide is carbonyldihydrazide.

13. A composition according to claim 1 in which the soap is a sodium soap and in which the hydrazide is lauric acid hydrazide.

14. A composition according to claim 1 in which the soap is a sodium soap and in which the hydrazide is stearic acid hydrazide.

15. A composition according to claim 1 also containing an amount of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenylmethane sufficient to impart bactericidal action to the soap.

References Cited in the file of this patent

UNITED STATES PATENTS

1,973,724	Perkins et al. _____	Sept. 18, 1934
2,014,924	Benedict _____	Sept. 17, 1935
2,535,077	Kunz et al. _____	Dec. 26, 1950
2,680,122	Black et al. _____	June 1, 1954
2,729,690	Oldenburg _____	Jan. 3, 1956
2,730,502	Beaver et al. _____	Jan. 10, 1956
2,808,416	Bell et al. _____	Oct. 1, 1957

FOREIGN PATENTS

423,938	Great Britain _____	Feb. 11, 1935
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OTHER REFERENCES

"Ind. and Eng. Chem.," July 1926, pp. 691-4, article by Smith.

Chemical Abstracts, vol. 26 (1932), page 5864.