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SODIUM SULFATE OF HIGHLY BRANCHED PRIMARY HEPTADECANOL

Walter M. Bruner, Wilmington, Del., assignor to
E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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1 Claim. (Cl. 260—459)

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This invention relates to novel sulfated primary alcohol compositions and more particularly to sulfated highly branched, primary heptadecanol compositions which are of value as surface-active agents.

For many years, important uses have existed for relatively high molecular weight alcohol sulfates, particularly those containing about 18 carbon atoms per molecule. To meet these important needs, especially in the detergent field, straight-chain alcohols have been manufactured on a rather large scale by hydrogenation of fatty acids or esters. In recent years the use of synthetic detergents, including those of the sodium alkyl sulfate type, has markedly increased, and at the same time supplies of natural fatty materials have become relatively scarce. The straight-chain primary alcohols have been difficult to synthesize in a practical way from low molecular weight, or readily available, non-fatty starting materials. Thus, a need has arisen for synthetic compositions which, like the long-chain alcohols obtained by hydrogenation of fats, would be useful as intermediates in the manufacture of surface-active agents, and it has become evident that this need could not be satisfied by the synthesis of straight-chain, synthetic, primary alcohols from non-fatty materials by previously known methods. Attempts have been made to employ certain synthetic branched-chain alcohols, especially secondary alcohols, in the manufacture of alcohol sulfate surface-active agents, and it has been reported that the secondary alcohols in which the alkyl groups are straight chain are markedly superior to those in which the alkyl groups are branched chain (U. S. 2,422,613; cf. also Ind. Eng. Chem. 35, 111 (1943)). Branched chain alcohols have been employed very successfully in the manufacture of the sodium dialkyl sulfocuccinate types of surface-active agent, but the alcohols employed in the latter processes are of relatively low molecular weight, and are not useful in making satisfactory sodium alkyl sulfates.

An object of the present invention is to provide, from readily available sources, primary alcohol sulfates which are suitable for use as surface-active agents, and which are useful for other purposes. Another object is to prepare a sulfated highly branched heptadecanol. Other objects of the invention will appear hereinafter.

The present invention provides, as novel compositions of matter, sulfates of a normally liquid, highly-branched primary heptadecanol. Since the heptadecanol of this invention is much more

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highly branched than any of the previously known primary alcohols of similar molecular weight, it is indeed quite remarkable that this heptadecanol can be converted to a sodium alkyl sulfate which has outstanding properties as a surface-active agent, and which, in fact, is far superior in wetting power to the best previously known sodium alkyl sulfates. This highly branched heptadecanol surface-active agent also differs from the previously known straight-chain sodium alkyl sulfates of similar molecular weight in that it is readily soluble in organic solvents. For example, it dissolves readily in hydrocarbons such as benzene which are non-solvents for the straight chain sodium alkyl sulfonates. The heptadecanol of this invention is further characterized in that it has a much lower boiling point than the previously known alcohols of similar molecular weight. It differs in physical form from the said previously known alcohols, and in fact is a liquid, rather than a solid, at ordinary temperatures.

The invention is further illustrated by means of the following example:

Tetraisobutylene (168.2 grams) was heated for two hours at a temperature of 200° to 230° C. in the presence of a cobalt naphthenate catalyst (0.5 gram) with a gas consisting of carbon monoxide and hydrogen (molar proportions, ca. 2:1) under a pressure of 500 to 700 atmospheres. After cooling to room temperature, the reaction mixture was discharged from the shaker tube and distilled. About 10% of the tetraisobutylene was depolymerized to diisobutylene. The fraction boiling between 80° and 143° C. at 3 mm. pressure was collected. Analysis of this fraction showed it to be mainly heptadecanol with a lesser amount of heptadecanal. This alcohol-aldehyde mixture was hydrogenated in dioxane solution at 150° to 165° C., at 700 atmospheres pressure, using a nickel-on-kieselguhr catalyst. Distillation of the resulting product gave a heptadecanol fraction which when purified by redistillation had a boiling point of 140° to 145° C./4 to 5 mm. This heptadecanol was converted to the sodium alkyl sulfate by reaction with chlorosulfonic acid for 35 minutes at 16° to 19° C. followed by neutralization with 14% aqueous sodium hydroxide. The aqueous solution thus obtained was dried on a drum drier to give a somewhat crude sticky solid. Another batch (20 grams) of the same heptadecanol was sulfated at 60° C., by reaction with 90% of the equivalent quantity of dioxane—SO₃ complex. The resulting sulfate was poured into 62.5 grams of a 5% aqueous sodium hydroxide

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solution, and the solution thus obtained was dried on a drum drier to give about 27 grams of nearly white flakes which amounted to 96% of the theoretical quantity of sodium heptadecyl sulfate. The product thus obtained had a sulfur content of 8.8% (theory for sodium heptadecyl sulfate, 8.9%); it was soluble in water, ethanol, ethyl ether, benzene and other organic solvents. This sodium alkyl sulfate was tested to determine its wetting power, i. e. the minimum concentration (grams/liter) in water which is required to cause a standardized skein of cotton to sink in 25 seconds. Comparative tests were made with well-known commercial surface-active agents. The results were as follows:

Results of wetting speed tests on various detergents

Detergent	Concentration of Detergent Required (grams/liter) to Wet Standard Cotton Skein in 25 seconds.	
	Distilled Water	Hard Water (hardness=360 p. p. m.)
sodium sulfonate from kerosene (No. 40 white oil).....	0.62	0.94
sodium "lorol" sulfate.....	1.2	1.8
sodium heptadecyl sulfate, prepared as described in this example.....	0.28	0.33

The tests set forth in Example 1 show that the sodium heptadecyl sulfate prepared from the heptadecanol of this invention is more effective in wetting cotton than commercially available surface-active agents of the sodium alkyl sulfate type.

It is to be understood that the foregoing example is illustrative only and that it should not be considered as limiting the invention. In the preparation of the C₁₇ aldehyde by carbonylation of tetraisobutylene, the CO:H₂ ratio may be varied rather widely, and any suitable hydrogenation catalyst may be employed as disclosed in copending application S. N. 598,208, filed June 7, 1945, now U. S. Patent 2,437,600, which issued March 9, 1948. Metallic cobalt, and cobalt salts, e. g. cobalt naphthenate, acetate, laurate, etc., have been employed successfully. Similarly, the C₁₇ aldehyde can be hydrogenated in the presence of any suitable hydrogenation catalyst without varying the nature of the C₁₇ alcohol which is obtained as a hydrogenation product. Any suit-

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able method may be employed for purifying the C₁₇ alcohol; for example, pure C₁₇ alcohol analyzing 98.2% to 99% heptadecanol by hydroxyl determination (boiling point, 110° to 118°/2 mm., R. I. 1.4561 to 1.4573 at 25° C.) was obtained by reacting the impure product (ca. 80%) with boric acid, removing volatiles from the resulting borate at low pressure, then recovering the pure alcohol by hydrolysis followed by distillation. The sulfation of the alcohol can be carried out by any suitable method, and the neutralization of the sulfate may be accomplished by employing ammonia, ethanolamine, diethanolamine, triethanolamine, morpholine, lime, calcium carbonate, magnesia, magnesium carbonate, alkali metal hydroxides or any other similar neutralizing agent. Since the procedure for carbonylation of tetraisobutylene, and for hydrogenation of the resulting C₁₇ aldehyde, may be varied rather widely without altering the properties of the heptadecanol thus obtained, it is to be understood that I do not limit myself except as set forth in the following claim.

I claim:

25 The sodium sulfate of a normally liquid, highly branched primary heptadecanol which heptadecanol has a boiling point in the range of 140° to 145° C., at a pressure of 4 to 5 mm., said heptadecanol being characterized further in that it is a hydrogenation product of the highly branched C₁₇ aldehyde obtained by simultaneous reaction of carbon monoxide and hydrogen with tetraisobutylene in the presence of a hydrogenation catalyst.

WALTER M. BRUNER.

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