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PREPARATION OF SUGAR ESTERS

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The present invention is directed to esters of polyols and more particularly to a novel and improved method of preparing partial esters of certain sugar polyols.

Generally, alcohols of low volatility can be esterified with a fatty acid by heating with the corresponding free acid in the presence of acid or alkaline catalysts or certain metallic salts. Furthermore, polyols, which are only slightly miscible with the fatty acids may have to be heated to very high temperatures in order to effect a certain solubility. The same applies to the production of partial esters by alcoholysis. This procedure cannot be used for the preparation of sugar esters since disaccharides will decompose even under the influence of only moderately high temperatures and they are very sensitive to strong acids or alkalis.

Thus, certain polyols do not lend themselves to the usual methods of esterification, as are commonly used in industrial practice. Generally, this is due to heat sensitivity of the polyols and their poor solubility in the molten fatty acid triglycerides or fatty alkyl esters or classical esterification solvents. To circumvent this difficulty, the reaction has been carried out using an acid chloride and the polyol in a special solvent or a combination of solvents with an acid-binding agent. Thus, a mixture of pyridine or anhydrous tertiary amine with chloroform, dimethyl formamide, or dimethyl sulfoxide with pyridine have been used. In these methods, anhydrous conditions are considered to be essential.

Another method of obtaining the esters has been by an alcohol interchange between methyl esters of fatty acids and sucrose with dimethyl formamide or dimethyl sulfoxide as a solvent and an alcohol alkoxide or alkaline carbonate as a catalyst.

These prior art methods have a number of disadvantages and offered a number of difficulties. The cost of the solvents is relatively high and a substantial amount of solvent is lost in the operation. Special apparatus is necessary to handle the large volume of solvents used and to maintain the required anhydrous conditions. There is also a personal hazard to the operators of the process due to the toxicity of the solvent. Similar difficulties are inherent in the use of the dimethyl formamide-pyridine process. In both cases, special and expensive apparatus is necessary and the complete elimination of the solvents presents a difficult technical problem. Furthermore, the pyridine-chloroform process does not yield partial esters but completely alkylated esters which do not possess a favorable hydrophylic-hydrophobic balance for surface-activity applications. For these obvious reasons, the process has not reached industrial scale.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior procedures of the type described, it being among the objects of the present invention to provide a method of making partial esters of polyols having 6 or more hydroxyl groups, which process is simple and effective, results in a high yield of product and requires only simple apparatus.

It is also among the objects of the present invention to provide a process which does not require solvents having measurable toxicity.

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It is further among the objects of the present invention to provide compositions containing partial esters of polyols with fatty acids, which are directly usable for industrial applications and after purification are usable for food purposes.

The present invention utilizes sugars as the polyols and reacts the same with alkyl carboxylic acid halides and more specifically with the acid chlorides of the higher fatty acids occurring in animal and vegetable oils and having from 8 to 22 carbon atoms. The operation is conducted in an alkaline medium in the presence of alkali metal hydroxides, carbonates or bicarbonates. The medium used is water so that the use of volatile organic solvents is avoided. It is well-known that said acid chlorides hydrolyze in aqueous media and it was therefore the opinion in the prior art that such hydrolysis would render esterification impractical. However, according to the present discovery, it has been found that although the reaction is conducted in aqueous phase, at least 40–50% of the acid chloride reacts to form polyol esters.

According to the present invention, contrary to commonly accepted concepts, the polyol is first dissolved in a small amount, preferably in one half to equal weight of water at room temperature. The solution is brought to an alkaline pH by the addition of concentrated aqueous alkali; then about an equimolecular amount of acid chloride is slowly added to the stirred mixture, concentrated alkali being added concurrently to maintain the pH of the mixture between 8 and 11. The temperature is usually maintained at about 40°–50° C. or lower. When the addition of the acid chloride is completed, the mixture is stirred for one to two hours. The slurry so obtained is then filtered or centrifuged, most of the unreacted polyol passing into the filtrate. The resulting solid is then dried at low temperature and preferably under vacuum. It contains on a dry basis between 20% and 50% of esters, the remainder being soap and sugar.

The unreacted sugar can be eliminated by suspending the mass in ice cold water, thorough agitation and subsequent filtration or centrifugation.

The present invention has a number of advantages over the prior methods used for making partial esters of said polyols. Simple equipment may be used and the equipment operated at a high capacity. The cycle of manufacture is short and the reaction proceeds rapidly and smoothly to completion.

The initial product of the reaction which is a mixture of polyol esters and soap, may be used directly for various operations such as, as a detergent or in combination with detergent builders. The composition is also useful in the neutral scouring and fulling of wool and as an aid in emulsifications.

The molar proportions of sucrose to acid chloride are not limited to a 1:1 ratio. Increased amounts of sucrose tend to form esters with a lower edgree of acyl substitution.

The invention is illustrated more specifically by the following examples of the operation thereof.

Example 1

342 parts of sucrose (1 mol) was dissolved in 70 parts by volume of water, the resulting syrup made alkaline by a 50% NaOH solution and 246 parts myristoyl chloride added slowly while the agitated mixture was kept alkaline by portion-wise additions of NaOH 50% aqueous solution. The temperature rose gradually to 50° C. and was kept there by water-cooling. When about 140 g. of acid chloride had been added the mixture became too thick for an efficient agitation. 450 parts by volume of water were then added portion-wise to maintain a fluid mixture. When all the acid chloride had been introduced, the mixture was agitated for another hour, ad-

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justed to pH 8 by addition of 12 parts acid chloride and agitated for another hour. The reaction mixture was then filtered giving a cake of 590 parts containing $68.5 \pm 3\%$ solids (435 parts solids).

The solids contain 29% soap (0.5 mol soap), 37% sugar esters, and about 34% sugar. The yield of sugar esters was 50% based on the acid chloride.

Example 2

171.0 parts sucrose (0.5 mol) were dissolved in 75 cc. H_2O , the syrup brought to pH 9 by addition of NaOH 50% aqueous solution and 137 parts of palmitoyl chloride (0.5 mol) added to the agitated mixture. The reaction mixture was kept alkaline by gradual addition of 64 parts of NaOH as a 50% solution. The mixture was kept fluid by gradual dilution with a total of 125 parts by volume H_2O . The temperature rose to about $50^\circ C$. and was maintained by cooling. When the addition of acid chloride was complete (1 hour) the mixture was agitated for another hour, then filtered on a vacuum filter. A cake weighing 397 parts was obtained. The water content of the cake was 31% (274 parts solids).

The dry solids contained 22-26% soap ($24 \pm 2\%$) or 65.8 ± 6 parts (0.2360 mol sodium palmitate), and 151 parts sugar. The yield of sugar esters was 58 ± 5 parts or $42.4 \pm 4\%$ based on the acid chloride.

We claim:

1. A method of making partial esters of sugar polyols having at least six hydroxyl groups which comprises dissolving said sugar polyol in an amount of water not more than the polyol, adding thereto an amount of an alkali taken from the class consisting of alkali metal hy-

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drides, carbonates and bicarbonates to provide a pH of about 8 to 11, introducing the chloride of a higher fatty acid having 8 to 22 carbon atoms in amount less than that necessary to completely esterify said polyol, the temperature of the reaction is not over about 40° to $50^\circ C$., whereby a reaction takes place forming partial esters of said sugar polyols.

2. A method according to claim 1 characterized in that the acid chloride is added continually and alkali is added concurrently to maintain the alkalinity of the mass.

3. A method according to claim 1 characterized in that the amount of water present being from one-half to an amount equal to that of the polyol.

4. A method according to claim 1 characterized in that the product is dissolved in an organic solvent in which soap is insoluble, and said esters are recovered from said solvent.

5. A method according to claim 1 characterized in that the product is acidified to release fatty acids from soap therein, is dissolved in an organic solvent in which soap is insoluble, and said esters are recovered from said solvent.

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