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[54] **BUILDERS FOR DETERGENT AND CLEANSING AGENTS**

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[52] **U.S. Cl.** ..... **252/96;** 252/89; 252/95; 252/99; 252/135; 252/DIG. 1; 252/DIG. 2; 252/DIG. 6; 260/485 G

[51] **Int. Cl.** **C11d 9/42**

[58] **Field of Search**..... 252/DIG. 1, DIG. 2, DIG. 6, 252/99, 135, 95, 96; 260/485 G

[56] **References Cited**

UNITED STATES PATENTS

3,655,645	4/1972	Jacques	260/485 G X
3,758,419	9/1973	Hayden et al.	252/135 X
3,761,412	9/1973	Lancelot et al.	252/135 X
3,763,231	10/1973	Bruson et al.	252/135 X

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[57] **ABSTRACT**

Water-soluble salts of acid carboxylic acid esters of bivalent aliphatic or olefinically unsaturated carboxylic acids or hydroxycarboxylic acids and at least trihydric aliphatic alcohols are used as builders for detergent and cleansing agents. Each hydroxylic group of the alcohol or optionally of the carboxylic acid has a carboxylic acid-molecule attached thereto.

2 Claims, 2 Drawing Figures

Fig. 1.

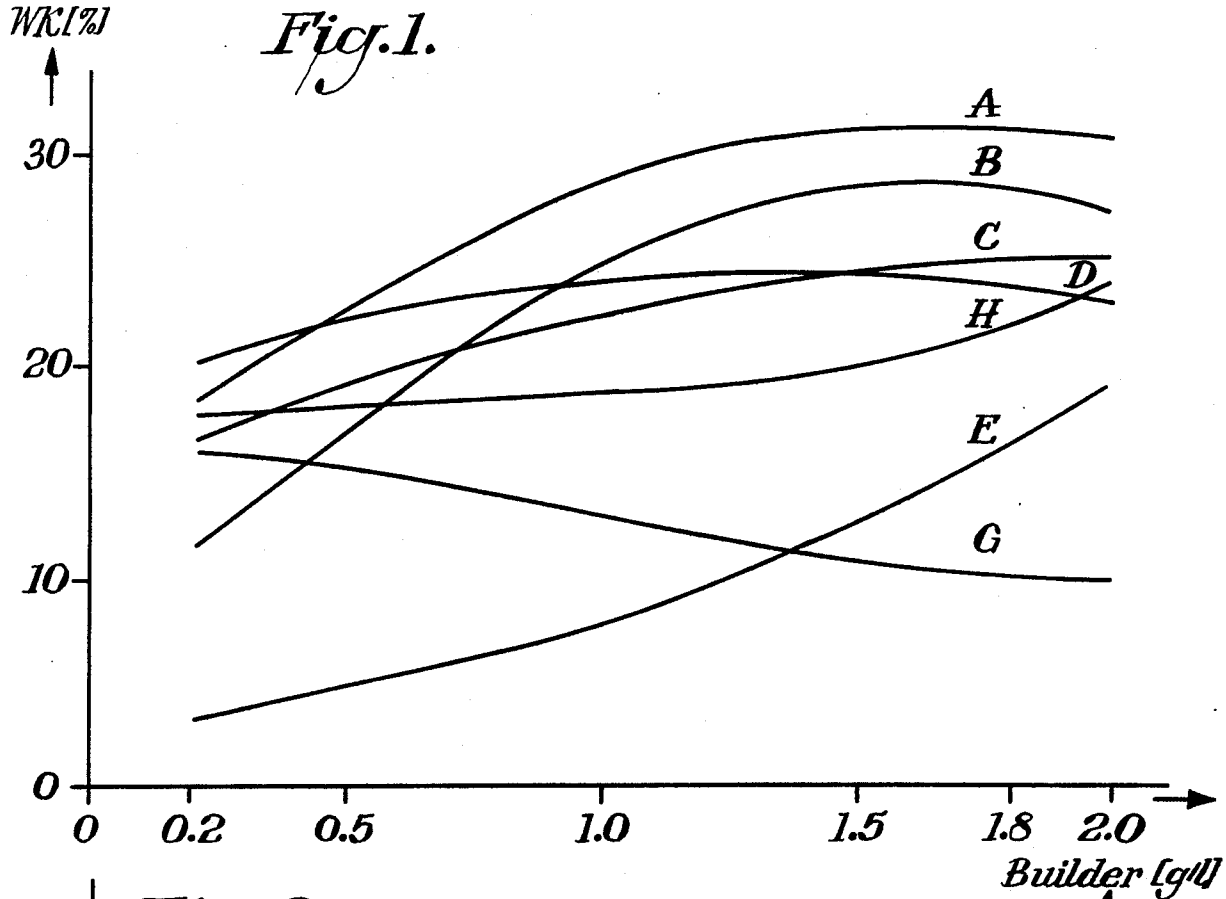
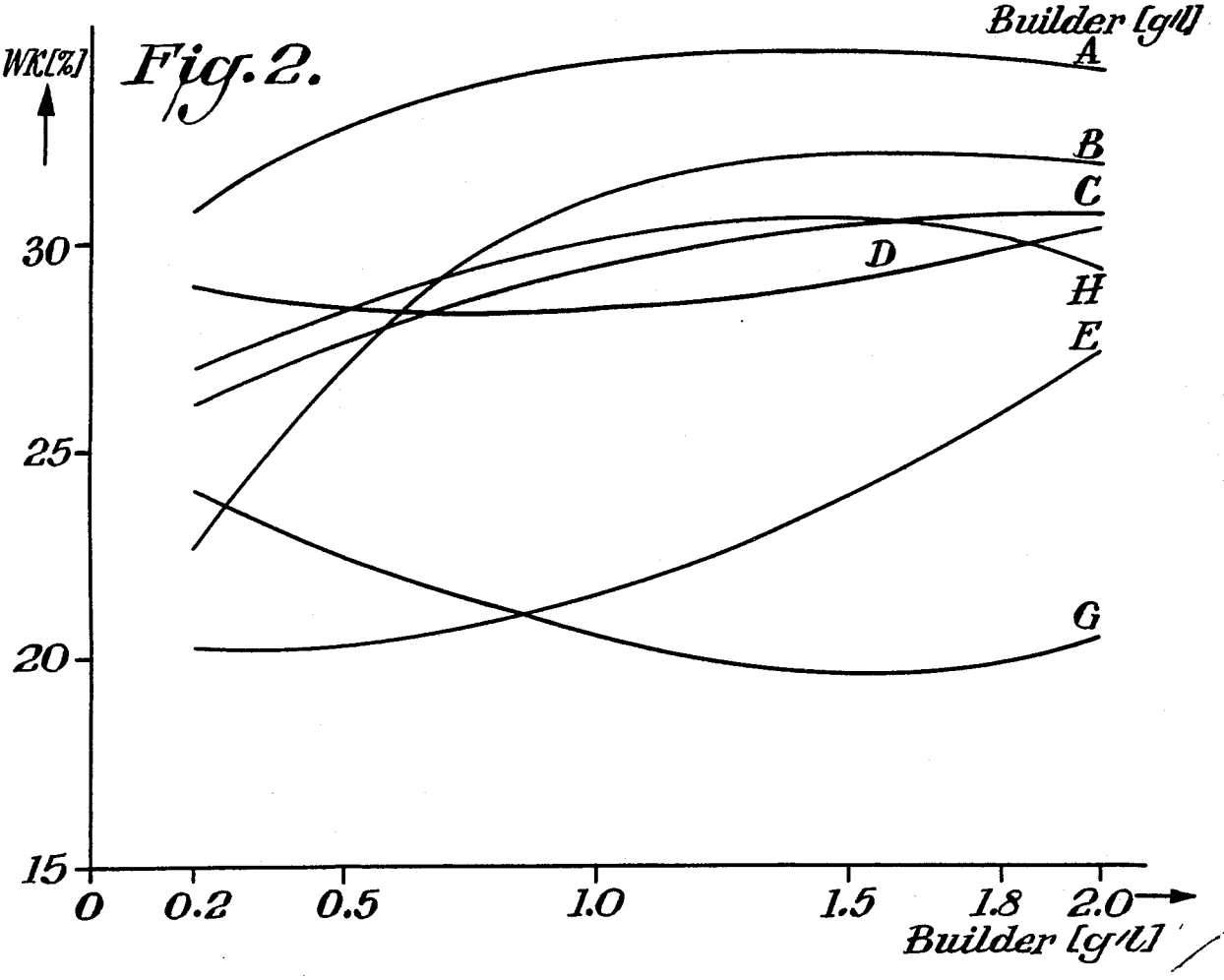

WK[%]
30
20
10
0
A
B
C
D
H
E
G
0
0.2
0.5
1.0
1.5
1.8
2.0
Builder [g/l]

Fig. 2.


WK[%]
30
25
20
15
A
B
C
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H
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0.2
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1.5
1.8
2.0
Builder [g/l]

BUILDERS FOR DETERGENT AND CLEANSING AGENTS

The present invention provides builders for detergents and cleansing agents, the builders comprising water-soluble salts of acid carboxylic acid esters and the esters being the product obtained by the reaction of bivalent carboxylic acids with polyhydric alcohols.

It has already been reported that the cleansing power of soaps and synthetic detergents in detergent and cleansing agents can be improved by means of certain addends. These cleansing intensifiers are termed builders. Detergent and cleansing agents having such builders therein are more effective, yet less costly than corresponding formulations which are free from builders.

The mechanism and the details of the "builder effect" have not yet been fully described. Vital to the function of the builder is a plurality of processes comprising, for example: the stabilization of pigment dirt suspensions; the emulsification of dirt particles; the effect on the surface and interfacial properties of aqueous tenside solutions; the solubilization of water-insoluble ingredients of the cleansing bath; the peptization of agglomerated dirt; the neutralization of acid substances; and the inactivation of mineral matter in the cleansing bath.

To determine the quality and qualification of individual materials for use as a builder, it is good practice to test their behaviour and efficiency in washing or cleansing operations, to ensure the qualitative and quantitative determination of all factors that make their contribution to the builder effect.

Classical builders comprise water-soluble inorganic alkali metal salts, such as alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, and silicates.

While a plurality of materials have been suggested for use as builders, the fact remains that linear condensed phosphates or polyphosphates, more particularly pentasodium triphosphate or sodium tripolyphosphate, are almost exclusively used as the builders in customary detergent and cleansing agents having up to substantially 50 weight percent builder therein.

The considerably increased consumption of phosphate-containing detergent and cleansing agents both for domestic and industrial purposes has also effected an increase in the phosphate content of natural waters. In studies of the eutrophication of waters, which has been found to occur at increasing rates, the nitrates and phosphates have recently been held to have properties that are able under certain conditions to promote the growth of certain alga species, and thereby to make their contribution to the eutrophication of water. Even though it is impossible for the time being definitely to clarify this problem, namely the contribution of detergents and cleansing agents to the eutrophication of water, it is highly desirable to have potential substitutes free from nitrogen and phosphorus for the builders, namely polyphosphates, that find widespread use in current detergent formulations.

Compounds which are free from nitrogen and phosphorus have already been suggested for use as builders in detergents. Starch derivatives, such as dicarboxyl and carboxymethyl starch, polycarboxylic acids, such as polymaleic acid and the copolymers thereof, oxydiacetic acid, oxydisuccinic acid, esters containing sulfonate groups of polyethylene glycol and adipic acid or

maleic acid, and esters of ethylene glycol and tri- or tetracarboxylic acids, have more particularly been used heretofore. The use of these substances as builders has been found to entail disadvantages which reside in the fact that they are insufficiently biodegradable or have an unsatisfactory power for dispersing hydrophilic dirt. Still further, there partially is a lack of processes permitting these substances to be made under commercially attractive conditions.

In addition to the tenside constituent, which merely enables hydrophobic dirt, such as carbon black and fat particles, to be dispersed and/or peptized, it is necessary for a detergent to contain a further ingredient removing hydrophilic dirt, namely a builder. In the absence of a builder, incrusted dirt on the fabric is but incompletely taken up by the cleansing bath and dirt particles are found to deposit on the fabrics. As a result, it is impossible to produce satisfactory cleansing effects.

We have now unexpectedly discovered that water-soluble salts of acid carboxylic acid esters produced from bivalent aliphatic or olefinically unsaturated carboxylic acids or hydroxycarboxylic acids and at least trihydric alcohols, each hydroxylic group of the alcohol and optionally of the carboxylic acid having a carboxylic acid-molecule attached thereto, are very suitable for use as builders in detergents and cleansing agents, as they have an efficiency excelling that of conventional builders free from nitrogen and phosphorus.

The cation of the water-soluble salts of acid carboxylic acid esters preferably is an alkali or ammonium ion, whereas the ester-type anion is based on a bivalent carboxylic acid, which has between 2 and 6 carbon atoms and is esterified with a polyhydric alcohol containing between three and six hydroxylic groups.

In accordance with the present invention, the acid component of the carboxylic acid esters should be selected, for example, from the group consisting of oxalic acid, malonic acid, maleic acid, succinic acid, oxydiacetic acid, tartaric acid, malic acid or itaconic acid, and the alcoholic component should be selected from the group consisting of glycerol, erythritol, pentaerythritol, mannitol, sorbitol or a sugar alcohol having between 4 and 6 carbon atoms.

To produce detergent and cleansing agents, it is possible to introduce the ester salt builders of the present invention into conventional detergent and cleansing agents, which are based on ion-active and/or non-ionic tensides and which may optionally contain further addends. In accordance with the present invention, the builder may generally be used in a proportion substantially between 10 and 80 weight percent, preferably between 15 and 60 weight percent, based on the dry substance of the detergent and cleansing agent. In addition to a water-soluble salt of acid carboxylic acid esters, the detergent and cleansing agents may contain as a further builder one or more alkali metal polyphosphates or their substitutes specified hereinabove. Detergent and cleansing agents prepared in accordance with the present invention give a pH-value between 8 and 12 in the aqueous medium of the wash bath.

The addends, which may be present together with the ion-active and/or non-ionic tensides in the detergents comprise substances, such as alkali metal or ammonium salts of sulfuric acid, silicic acid, di- and trisilicic acids, carbonic acid, boric acid, iminodiacetic acid, nitrilotriacetic acid, ethylene diamine tetracetic acid, al-

kylene phosphonic acids, hydroxyalkylene phosphonic acids and/or aminoalkylene phosphonic acids, or stabilizers and activators for perborates, as well as optical brighteners, carboxymethyl cellulose, magnesium silicate, disinfectants and/or enzymes, for example.

The carboxylic acid esters underlying the builder salts of the present invention are produced by conventional esterification methods, for example, by reacting the acid with the alcohols and simultaneously removing the reaction water by means of an expelling agent. The acid and alcohol should generally be used in a molar ratio such that one molecule of the bivalent carboxylic acid be available, per alcoholic hydroxylic group. In those cases in which the carboxylic acid itself contains one or more hydroxylic groups, it is also possible to esterify these groups. In this case, the quantitative ratio between acid and alcohol is accordingly greater than the number of the hydroxylic groups in the polyhydric alcohol. During the esterification, it is necessary and critical to remove from the esterification mixture one mol of reaction water, per mol of carboxylic acid used. The resulting acid carboxylic acid esters are transformed into water-soluble salts by the addition of stoichiometric proportions of alkali.

The builders of the present invention offer technically very beneficial effects as they considerably delay the precipitation of calcium ions in the wash bath and additionally do form stable dispersions with hydrophilic pigment particles. A further beneficial effect resides in the fact that they are readily biodegradable and thereby prevented from concentrating in natural waters.

The properties of the builders of the present invention can be evaluated, for example, by identifying their power of dispersing iron (III) oxide, their power of binding calcium ions and their washing efficiency on washing an artificially soiled fabric. Suitable tests were made with the builders of the present invention and the results obtained were compared wtih the properties of conventional builders. The tests were more particularly carried out in the manner described in the following Examples.

EXAMPLE 1

The following novel builders:
A: Sodium salt of glycerol-tri-oxydiacetic acid
B: Sodium salt of sorbitol-hexa-oxydiacetic acid
C: Sodium salt of glycerol-tri-malic acid
were tested as to their dispersing effect in an aqueous suspension of 4 weight percent of dry, pulverized iron (III) oxide with a particle size of less than 0.058 mm, and the effect produced was compared with that produced by conventional builders, namely:
D: Oxydiacetic acid
E: Malic acid
F: Glycerol
G: Diacetin
H: Sodium salt of citric acid ethyleneglycol ester.
Each of the builder was used in the suspension in a concentration of 0.16 weight percent, based on the aqueous solution. The settling time of the iron oxide particles in 25 cc mixing cylinders, and the volume of sedimentation after 24 hours were determined in each case as an index of the dispersing effect. The suspension had a pH-value of 10. The results obtained are summarized in Table 1 below.

Table 1

Builder	Sedimentation volume in milliliters	Settling time in hours
A	1.40	20
B	1.45	18
C	1.40	17
D	unstable	unstable
E	unstable	unstable
F	unstable	unstable
G	unstable	unstable
H	1.5	16

As can be seen from Table 1, the novel builders had a dispersing effect on hydrophilic dirt particles which was better than that of conventional builders. This results from both the smaller sedimentation volume and lower settling rate.

EXAMPLE 2

The builders specified in Example 1 were tested as to their power of binding calcium ions. The power of binding calcium ions in an aqueous solution is defined by the number identifying the grams of calcium ions kept in solution under certain conditions, by 100 grams of builder. This number is determined by titration with sodium carbonate. More particularly, a 1 percent test solution with a pH-value of 10 was titrated with a **0.1N** calcium chloride solution until turbidity commenced to occur. The following numerical values indicating the power of binding calcium ions were determined for the individual builders (Table 2).

TABLE 2

Builder	Power of binding Ca-ions (g Ca^{++} / 100 g builder)
A	11.1
B	10.2
C	3.6
D	15.5
E	—
F	—
G	—
H	3.0

As can be seen from Table 2, the novel builders were found to combine the good dispersibility of Table 1 with a good power for binding Ca^{++}-ions. As compared therewith, conventional builders could not be found to have these two properties at the same time to the same extent.

EXAMPLE 3

Wash tests were made to determine the cleansing power quotients of wash liquors which for a constant concentration of surface active substance contained varying proportions of the builders of the present invention specified in Example 1, and the test results obtained were graphically plotted in FIG. **1** of the accompanying graphs, curves A–C. Analogous wash tests with the use of the conventional builders, specified in Example 1, were made for the purpose of comparison, and the cleansing power quotients were also graphically plotted in FIG. **1**, curves D, E, G and H.

The wash tests were made on standard cotton fabrics soiled with "Krefeld" dirt in a "Launder-O-meter" at a wash bath temperature of 95°C. Standard fabrics soiled with Krefeld dirt have been defined by Kurt Lindner in the book entitled: "Tenside, Textilhilfsmit-

tel - Waschrohstoffe", Wissenschaftl. Verlagsgesellschaft Stuttgart (1964), volume II, page 1837.

The wash water had a hardness of 20° (German degrees of hardness) and a pH of 10. The wash period was 30 minutes and the bath ratio, expressed by the ratio of material to be washed in kg to wash liquor in liter was 1:50, and the wash operation was carried out in the presence of 10 steel balls. The wash liquor contained as surface-active substances

0.45 g/liter of dodecylbenzene sulfonate,
0.15 g/liter of tallow fatty oil and
0.15 g/liter of hardened tallow soap.

The builders were used in the wash liquor in a concentration between 0.2 and 2 grams/liter of wash liquor.

After the prescribed wash time, the standard cotton fabric was rinsed, once hot and once cold, and its degree of whiteness was then determined using an Elrepho remission photometer, (a product of Zeiss) and a filter R 53. Based on the test result obtained, the cleansing power quotient was calculated according to the following formula:

$$\% \text{ WK} = \% \text{ WG}_{\text{"}} - \% \text{ WG}_{\text{'}}$$

in which % WK = % cleansing power,
% $WG_{"}$ = % whiteness of washed fabric,
% $WG_{'}$ = % whiteness of unwashed fabric.

As can be seen from curves A–C shown in FIG. 1, more cleansing power is imparted to the wash liquor by the builder employed in accordance with the present invention than by the conventional builders D, E, G and H.

EXAMPLE 4

The procedure was the same as that described in Example 3, save that the following additional ingredients were introduced into the wash liquor;

0.15 g of magnesium silicate/liter of wash liquor,
0.15 g of sodium silicate/liter of wash liquor,
1.25 g of sodium perborate tetrahydrate/liter of wash liquor,
0.45 g of sodium sulfate/liter of wash liquor, and
0.05 g of Tylose/liter of wash liquor.

The wash results obtained were graphically plotted in FIG. 2, curves A–C. As can be seen, the builders used in accordance with the present invention were found to distinguish favorably over the conventional builders (curves D, E, G and H).

PREPARATION OF THE BUILDERS USED IN ACCORDANCE WITH THIS INVENTION.

The builders used in Examples 1 to 4 were not specifically purified during preparation. In other words, the reaction products (crude products) directly obtained following termination of the esterification of the polyvalent carboxylic acid with the polyhydric alcohol and following neutralization of the resulting esterification mixtures, were used. This is further illustrated in the following Examples.

EXAMPLE 5

A mixture of 92 parts by weight of glycerol and 402 parts by weight of oxydiacetic acid was subjected to azeotropic distillation with 250 parts by weight of toluene, which was continuously recycled, so as to remove 54 parts by weight of reaction water, which did form during the esterification. The mixture was cooled and the toluene was separated from the ester layer. To produce the sodium salt, the acid crude ester was neutralized with 300 parts by weight of 40 percent sodium hydroxide solution and the resulting neutralization mixture was dried under vacuum. The product so obtained was used as builder A in Examples 1 to 4.

EXAMPLE 6

A mixture of 182 parts by weight of sorbitol and 804 parts by weight of oxydiacetic acid was subjected to azeotropic distillation with 250 parts by weight of toluene, which was continuously recycled, so as to remove 180 parts by weight of reaction water. The ester was cooled and the toluene was separated from the ester layer. To produce the sodium salt, the crude ester was neutralized with 600 parts by weight of 40 percent sodium solution and the resulting neutralization mixture was dried under vacuum. The product so obtained was used as builder B in Examples 1 to 4.

We claim:

1. A detergent composition containing dodecylbenzene sulfonate, tallow oil, hardened tallow soap, magnesium silicate, sodium silicate, sodium perborate tetrahydrate, sodium sulfate, and a builder, the builder being a substance selected from the group consisting of the sodium salt of glycerol-trioxydiacetic acid, the sodium salt of sorbitol-hexaoxydiacetic acid and the sodium salt of glycerol trimalic acid, the builder being present in a proportion between 10 and 80 weight percent based on the total dry ingredients of the composition.

2. The detergent composition according to claim 1 wherein the builder is present in an amount between 15 and 60 weight percent and the composition additionally contains an alkali metal polyphosphate builder.

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