

PATENT SPECIFICATION

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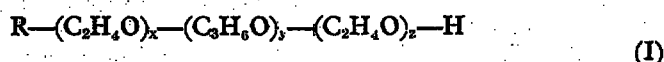
(54) PROCESS OF THE PRODUCTION OF POLYGLYCOLETHER COMPOUNDS AND THEIR USE

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polyalkylene oxide adducts, a process for their manufacture, their use as scouring or washing agents (especially for textile articles, e.g. such as have been dyed, for instance with a disperse dye), as wetting agents (e.g. in textile treatment, for instance dyeing, baths), and their aqueous solutions.

The use of polyalkylene oxide adducts as scouring agents and as dyeing assistants is known. It is desirable that these products should foam a little as possible, especially when employed in jet dyeing machines, while at the same time they should exercise efficient wetting and detergent action. It has been found that polyalkylene adducts as identified below have little tendency to foam and have powerful wetting and detergent action.

The present invention provides a polyglycol ether compound of the formula



where

R represents an alkoxy or aralkoxy radical containing 8 to 24 carbon atoms,

x represents an integer from 5 to 11,

y represents an integer from 5 to 18,

and

z represents an integer from 8 to 20,

The present invention also provides a process for the production of a polyglycol ether, which comprises reacting an alcohol of the formula



(II)

with ethylene oxide, then with propylene oxide and subsequently with ethylene oxide in the molar ratio 1:x:y:z, respectively, wherein the symbols R, x, y and z are as defined above.

Preferably the radical R contains 11 to 15 carbon atoms. It is preferably a secondary alkoxy radical. The value of x is 5 to 11, preferably 9 or 10, that of y is 5 to 18, preferably 12 to 17 or more especially 15 or 16, and that of z 8 to 20, preferably 8 to 12.

Above all the quantitative relation of the sum total of the ethylene oxide to that of the propylene oxide is important, though notably good results are obtained with the ratio x:y:z as noted above. It will be appreciated that in the process of the in-

vention a mixture of products may be produced so that the values of x, y and z may be average values, especially if a mixture of alcohols of formula (II) is employed. Examples of the radical as defined above are alkoxy radicals with, as the alkyl component, octyl, decyl, undecyl, heptadecyl, octadecyl, iso-octyl, iso-decyl and iso-heptadecyl, and aralkoxy radicals such as phenylethoxy and phenylpropoxy.

Oxalkylation with ethylene and propylene oxide can be carried out advantageously at elevated temperature, for example above 100°C, preferably at 140° to 200°C and more preferably at 170—180°C, if necessary in the presence of an alkaline or acid catalyst such as sodium or potassium hydroxide or carbonate, antimony pentachloride, stannous tetrachloride or boron trifluoride etherate. The reaction can be conveniently carried out in the absence of air, for example by the introduction of nitrogen gas, if desired at excess but preferably at normal pressure. The reaction is preferably terminated by introducing nitrogen into the reaction mixture.

The products obtained are soluble in water and are marketed and used preferably in the form of concentrated aqueous solutions, for example of 60—70% strength, by weight.

Aqueous solutions of compounds of formula (I) show little or no foaming, are stable to acids, dyes and salts, and are highly suitable for washing or scouring textiles and textile fibres, especially for scouring such textile materials before dyeing or printing and for washing off such textile materials after dyeing or printing. The textile materials may be in any of the forms occurring in textile production, for example loose fibres, filament, yarn, nonwovens, felts, carpets, woven and knitted fabrics, and may consist of synthetic, semi-synthetic or natural high polymers. The following may be named as examples of such textile materials: natural and regenerated cellulosic fibres, polyamide fibres including wool, silk and synthetic polyamides, polyacrylonitrile, polyester and polyolefin fibres, of which polyester, wool and blend fabrics of polyester and cotton or polyamide and polyacrylonitrile fibres are especially notable. As is well-known, the above-mentioned scouring process is normally necessary to remove contaminants, e.g. oil, fats, and various other impurities, from textile materials prior to dyeing or printing, thus ensuring optimum take-up of the dye. The washing off process is often necessary to remove excess dye and other impurities, e.g. dyebath additives such as carriers, from the dyed or printed textile materials, prior to drying.

The aqueous solutions used e.g. in a bath for scouring or washing off contain as sole low-foaming or non-foaming detergent a compound of formula (I), for example in amounts of 0.01 to 2% by weight, preferably 0.05 to 0.2% by weight. These solutions are also highly suitable for use as wetting agents and in particular as dyeing assistants, for example in the dyeing of hydrophobic textiles with disperse dyes. A special merit of the invention is that it enables textiles to be scoured with aqueous solutions of compounds of formula (I) and then dyed or printed in the same medium after the addition of dye, or alternatively scoured and dyed or printed simultaneously. These solutions, regardless of their detergent action, can be used as assistants in dyeing and printing, for example with disperse and/or reactive dyes. It is to be noted that the compounds of formula (I) can be used in substantially smaller amounts for this purpose than for scouring and washing off.

Textiles which have been treated with compounds of formula (I) in wet processing, either before, during or after dyeing or printing, have the full fastness properties of the dyes used, notably the full rubbing fastness. Further advantages are offered by the compounds including suitability for use in scouring in jet dyeing machines, in particular the Gaston County Jet dyeing machines, as they develop little or no foam and have notable wetting and detergent action; minimal foam formation in disperse dyebaths which results in little or no dye being retained in the bath; and the achievement of notable white reserve shown by the unprinted areas in prints with disperse dyes after washing off.

The following Examples illustrate the invention further without limiting its scope. The parts and percentages are by weight and the temperatures in degrees Centigrade.

Example 1 (Production of Assistant I)

In the presence of 0.5% sodium hydroxide as catalyst, 928 parts (16 mols) of propylene oxide are added on 598 parts of a secondary C₁₁—C₁₅ alcohol mixture previously reacted with 9 mols of ethylene oxide, after which 440 parts (10 mols) of ethylene oxide are added on, working at 170—180° throughout under normal pressure. The first addition reaction is carried out by slowly dropping the propylene oxide

into the alcohol mixture in the absence of air and with thorough stirring. The second addition reaction is effected by introducing the liquid ethylene oxide into the propoxylated mixture and is completed by directing nitrogen into the mixture in place of ethylene oxide. The reaction mixture is then allowed to cool. Assistant I is obtained. It is free from foaming and has excellent detergent and wetting action for hydrophobic and natural textile fibres. The turbidity point of a 1% solution of the product is 43°.

Example 2

(Production of Assistant II)

In analogy with Example 1, 526 parts of octanol-(2), previously reacted with 9 mols of ethylene oxide, are reacted with 928 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide. The product is Assistant II. Octanol-(2) can be replaced by a primary octyl alcohol, whereby assistant IIa is obtained.

Example 3

(Production of Assistant III)

638 Parts of hexadecanol-(2) reacted with 9 mols of ethylene oxide are reacted with 328 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide as described in Example 1. Assistant III is obtained.

Example 4

(Production of Assistant IV)

582 Parts of dodecanol-(2) reacted with 9 mols of ethylene oxide are reacted with 928 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide as described in Example 1. Assistant IV is obtained. The dodecanol-(2) can be replaced by dodecanol-(1), whereby Assistant IVa is obtained.

Example 5

(Production of Assistant V)

554 Parts of decanol-(2) reacted with 9 mols of ethylene glycol are reacted with 928 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide by the procedure of Example 1 to give Assistant V. The reaction can be carried out in an analogous manner using 722 parts of behenyl alcohol reacted with 9 mols of ethylene oxide, or octadecanol-(1) in place of decanol-(2). The products are Assistants Va and Vc respectively.

Example 6

(Production of Assistant VI)

610 Parts of tetradecanol-(2) reacted with 9 mols of ethylene oxide are reacted with 928 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide as described in Example 1. The product is Assistant VI. The tetradecanol-(2) can be replaced by tetradecanol-(1) which results in Assistant VIa.

Example 7

(Production of Assistant VII)

420 Parts of a secondary $C_{11}-C_{15}$ alcohol mixture reacted with 5 mols of ethylene oxide are reacted with 928 parts (16 mols) of propylene oxide and 440 parts (10 mols) of ethylene oxide as described in Example 1. Assistant VII is obtained.

Example 8

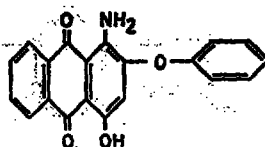
(Production of Assistant VIII)

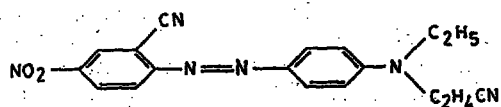
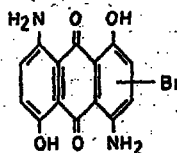
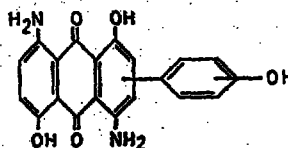
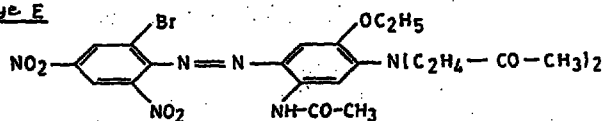
526 Parts of a secondary $C_{11}-C_{15}$ alcohol mixture reacted with 9 mols of ethylene oxide are reacted in analogy with Example 1 with 1044 parts (18 mols) of propylene oxide and 880 parts (20 mols) of ethylene oxide. Assistant VIII is obtained.

Examples of Application

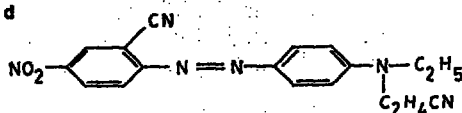
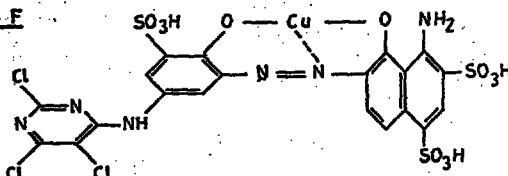
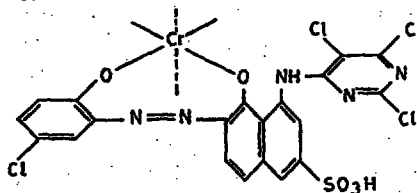
The dyes used to perform the following Examples have the formulae given below.

Dye A

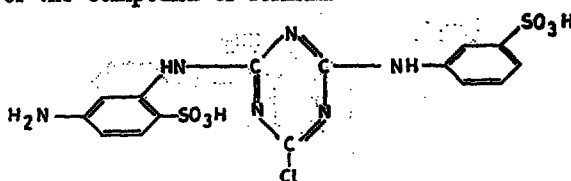


Dye BDye CDye DDye E

and

Dye FDye GDye H

This is produced in accordance with German Patent 1 039 992, column 5, lines 47—53, or by reaction of 1 mol of copper phthalocyanine tetrasulphonic acid chloride with 1—2 mols of the compound of formula



Example 9

Washing off prints produced with disperse dyes:

A 67/33% polyester/cotton blend fabric is printed with 1000 parts of a paste containing 120 parts of dye B. The printed fabric is rinsed in the Launder-Ometer for 15 minutes with cold water, liquor ratio 100:1, and then washed off with 15 minutes at 60° with 2 g/l of Assistant I. The unprinted areas of the fabric are reserved white. If washed off without Assistant I, the unprinted parts of the fabric are stained by the dye.

Example 10

Example 9 is repeated with the same success using in place of dye B the same amount of dye C.

Example 11

The polyester/cotton blend fabric of Example 9 is replaced by acetate twill, triacetate satin, polyester fabrics, and the procedure of that Example repeated with equal success.

Example 12

A 50/50% polyamide/cellulose triacetate blend fabric is printed with 1000 parts of a paste containing 120 parts of dye C. The printed fabric is washed off at liquor ratio 20:1 in a bath set with a low-foaming detergent containing 0.2% of Assistant I, first for 30 seconds at room temperature, then for 60 seconds at room temperature and 60 seconds at 40°. The unprinted areas of the fabric are left with a white reserve.

Example 13

Combined scouring and dyeing procedure:

A textured polyester fibre, not previously scoured or set, is rinsed with cold water for a short time in the Gaston County jet dyeing machine. Then 0.5 g/l of Assistant I is added and the rinsing water is heated to 70° at pH 9-10. The pH is adjusted to 5, the bath is set with 0.5% of dye A and its temperature raised to 125°. The fabric is dyed at this temperature for 45 minutes, rinsed and thermofixed at 150°. A level dyeing is obtained. No interference from foam occurs in scouring or dyeing.

Level dyeings are obtained when in place of Assistant I similar amounts of Assistant II, IIa, III, IV, IVa, V, Va, Vc, VI, VIa, VII or VIII are present in the bath and one of the dyes B to G is employed in place of dye A.

Example 14

Detergent power:

A 10 gramme sample of a grey polyester fabric containing 5.8% oil is scoured in the Lintest apparatus for 30 minutes at 70° and liquor ratio 30:1 with 1 g/l of Assistant I and 2 g/l tetrasodium pyrophosphate (pH ≈ 10). After subsequent rinsing its residual oil content is 0.3%.

Comparable scouring action is obtained when the bath is set with 2 g/l ammonium sulphate and acetic acid (pH ≈ 5.5) in place of 2 g/l tetrasodium pyrophosphate.

Example 15

An artificially soiled cotton fabric is scoured for 30 minutes at 95° in a bath containing 0.05% to 0.4% of the polyadduct described in Example 1 and 0.2% sodium carbonate. The fabric is photoelectrically measured before and after scouring and the difference in whiteness noted as a measure of the power of detergency. The product develops practically no foam, but it has excellent wetting and scouring action.

Example 16

a) A wool fabric is dyed at liquor ratio 40:1 in a bath containing 3% of dye H, 1.5% acetic acid, 10% sodium sulphate and 1% of Assistant I relative to the fabric weight.

b) The wool is first treated for 10 minutes at 50° in the bath without dye, after which the well dissolved dye is added. The bath is then brought to the boil in 45 minutes and the fabric dyed for 45 minutes at the boil. A level dyeing is obtained. Dyeings on wool showing comparable levelness are obtained with the aid of Assistants II, VI and VIII. If no assistant of the disclosed type is present in the bath, the dyeing is unlevel.

Example 17

High-temperature dyeing of polyester fabric:

- 100 Parts of an unset polyester fabric are dyed for 30 minutes at 130° in an aqueous bath of 6000 parts containing 1.8 parts of the dye used in Example 3, 12 parts of ammonium sulphate and 2 parts of the compound described in Example 1. The polyglycolether is stable under high-temperature conditions in the presence of disperse dyes. After dyeing, the fabric is rinsed and washed off as in Example 2. A level dyeings with very good rubbing fastness is obtained.

Example 18

- A fabric of textured polyester yarn contaminated with 6% of preparative oils scoured for 30 minute at 70° in the Gaston County jet dyeing machine in an aqueous bath containing 0.1% of the polyadduct of average molecular weight 1800—2000 described in Example 1. The scouring bath is allowed to cool to 60° and the fabric rinsed. It is then dyed for 1 1/2 hours at 120° in a bath set with about 1.5% of dye C, 3% aminosodium phosphate and 5% of a carrier containing 80% ortho-phenylphenol and 20% emulsifier. The dyebath is cooled to 65° and the fabric rinsed and washed off for 20 minutes at 80° with 0.6% of the compound described in Example 1. 2% of caustic soda flakes and 3% sodium hydrosulphite. After the scouring bath has cooled to 65° the fabric is rinsed for 10 minutes with water. No interfering foam appears during scouring. The excellent detergent action prevents spot formation on the dyed fabric.

WHAT WE CLAIM IS:—

1. A polyglycol ether compound of the formula



- in which

R represents an alkoxy or aralkyloxy radical containing 8 to 24 carbon atoms,
x represents an integer from 5 to 11,
y represents an integer from 5 to 18,

and

z represents an integer from 8 to 20.

2. A polyglycol ether compound according to Claim 1, in which R represents a secondary alkoxy radical containing 8 to 24 carbon atoms.
3. A polyglycol ether compound according to Claim 1 or Claim 2, in which R represents an alkoxy radical containing 11 to 15 carbon atoms.
4. A polyglycol ether compound according to any preceding claim, in which x is 9 or 10.
5. A polyglycol ether compound according to any preceding claim, in which y is 12 to 17.
6. A polyglycol ether compound according to Claim 5, in which y is 15 or 16.
7. A polyglycol ether compound according to any preceding claim, in which z is 8 to 12.
8. A polyglycol ether compound according to Claim 1, substantially as herein described with reference to any one of Examples 1 to 8.
9. A concentrated aqueous solution of a compound as claimed in any preceding claim, of 60—70% strength by weight.
10. A process for the production of a polyglycol ether compound as defined in Claim 1, which comprises reacting an alcohol of the formula

RH

(II)

- with ethylene oxide, then with propylene oxide, and subsequently with ethylene oxide in the molar ratio 1:x:y:z, respectively, wherein the symbols R, x, y and z are as defined in Claim 1.

11. A process according to Claim 10, substantially as herein described with reference to any one of Examples 1 to 8.

12. A polyglycol ether compound whenever produced by the process according to Claim 10.

13. A process for washing or scouring a textile material, which comprises using as the washing or scouring agent a compound as claimed in any one of Claims 1 to 8 and 12 in aqueous solution.

Example 17

High-temperature dyeing of polyester fabric:

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Example 18

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WHAT WE CLAIM IS:—

1. A polyglycol ether compound of the formula



in which

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x represents an integer from 5 to 11,

y represents an integer from 5 to 18,

and

z represents an integer from 8 to 20.

2. A polyglycol ether compound according to Claim 1, in which R represents a secondary alkoxy radical containing 8 to 24 carbon atoms.

3. A polyglycol ether compound according to Claim 1 or Claim 2, in which R represents an alkoxy radical containing 11 to 15 carbon atoms.

4. A polyglycol ether compound according to any preceding claim, in which x is 9 or 10.

5. A polyglycol ether compound according to any preceding claim, in which y is 12 to 17.

6. A polyglycol ether compound according to Claim 5, in which y is 15 or 16.

7. A polyglycol ether compound according to any preceding claim, in which z is 8 to 12.

8. A polyglycol ether compound according to Claim 1, substantially as herein described with reference to any one of Examples 1 to 8.

9. A concentrated aqueous solution of a compound as claimed in any preceding claim, of 60—70% strength by weight.

10. A process for the production of a polyglycol ether compound as defined in Claim 1, which comprises reacting an alcohol of the formula

RH

(II)

with ethylene oxide, then with propylene oxide, and subsequently with ethylene oxide in the molar ratio 1:x:y:z, respectively, wherein the symbols R, x, y and z are as defined in Claim 1.

11. A process according to Claim 10, substantially as herein described with reference to any one of Examples 1 to 8.

12. A polyglycol ether compound whenever produced by the process according to Claim 10.

13. A process for washing or scouring a textile material, which comprises using as the washing or scouring agent a compound as claimed in any one of Claims 1 to 8 and 12 in aqueous solution.



14. A process according to Claim 13, in which the textile material is scoured before dyeing or printing.
15. A process according to Claim 13, in which the textile material is washed off after dyeing or printing.
- 5 16. A process according to Claim 13, in which the textile material is scoured and then dyed or printed in the same medium after the addition of a dye. 5
17. A process according to Claim 13, in which the textile material is scoured and dyed or printed simultaneously.
- 10 18. A process according to any one of Claims 13 to 17, in which the aqueous solution of the compound as claimed in any one of Claims 1 to 8 and 12 contains 0.01 to 2% by weight of that compound. 10
19. A process according to Claim 18, in which the aqueous solution contains 0.05 to 0.2% by weight of the compound.
- 15 20. A process according to any one of Claims 13 to 19, in which the textile material consists of synthetic, semi-synthetic or natural high polymers. 15
21. A process according to Claim 15, substantially as herein described with reference to any one of Examples 9 to 12.
22. A process according to Claim 13, substantially as herein described with reference to either one of Examples 13, 16a) and 17.
- 20 23. A process according to Claim 13, substantially as herein described with reference to either one of Examples 14 and 15. 20
24. A process according to Claim 16, substantially as herein described with reference to Example 16b.
- 25 25. A process according to Claims 14 and 15, substantially as herein described with reference to Example 18. 25
26. A textile material whenever treated according to the process claimed in any one of Claims 13 to 25.
- 30 27. A process for assisting the dyeing or printing of a textile material, which comprises using as the dyeing or printing assistant a compound as claimed in any one of Claims 1 to 8 and 12. 30
28. A process according to Claim 27, in which a hydrophobic textile is dyed with a disperse dye in the presence of the dyeing or printing assistant.

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