

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 019 484
B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **30.03.83**

(51) Int. Cl.³: **C 11 D 1/66, C 11 D 3/37,
C 11 D 17/00**

(21) Application number: **80301650.0**

(22) Date of filing: **20.05.80**

(54) **Compositions containing nonionic surfactants and a process for producing them.**

(30) Priority: **21.05.79 GB 7917636**

(43) Date of publication of application:
26.11.80 Bulletin 80/24

(45) Publication of the grant of the patent:
30.03.83 Bulletin 83/13

(84) Designated Contracting States:
AT DE FR GB IT SE

(56) References cited:
**DE - A - 2 747 602
US - A - 3 682 849**

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Courier Press, Leamington Spa, England.

EP 0 019 484 B1

Compositions containing nonionic surfactants and a process for producing them

This invention relates principally to detergent powders containing a nonionic surfactant as the major detergent active compound. It also relates to a process for preparation of such detergent powders.

We have now filed a number of patent applications concerned with increasing the stability of detergent formulations during processing. Solutions to the problem have largely been concerned with addition to the detergent slurry of nitrogen-containing compounds such as alkanolamides, amines and quaternary ammonium salts. In practice a nitrogen compound of this sort helps to inhibit autoxidation which is the main problem which arises during processing, and also helps to inhibit any tendency to decomposition during storage after manufacture has been completed.

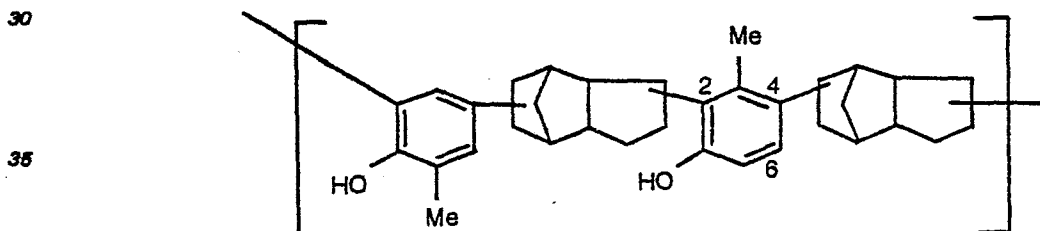
US Patent No. 3,403,107 discloses the use of antioxidants for inhibition of smoke formation during spray-drying of nonionic surfactants and more significantly discloses a large number of phenolic antioxidants, including some which are substituted *bis* phenols.

We have now discovered that one particular phenolic antioxidant which is not disclosed in the above US Patent has an exceptional effect in inhibiting oxidation of detergent slurries containing nonionic surfactants.

According to its broadest aspect, the invention provides a composition comprising from 2 to 50% by weight of a nonionic surfactant in the form of a C_6-C_{24} primary or secondary alcohol ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol and from 0.001 to 0.5% by weight of a phenolic antioxidant, characterised in that the phenolic antioxidant comprises a copolymer of dicyclopentadiene with a mixture of 2- and 3-methyl phenols.

In a second aspect, the invention provides a process for the manufacture of a detergent powder which comprises forming an aqueous slurry comprising an amount of a nonionic surfactant in the form of a C_6-C_{24} primary or secondary alcohol ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol sufficient to provide from 2 to 50% by weight of the surfactant in the spray-dried powder and a minor amount of a phenolic antioxidant, and spray-drying it characterised in that the phenolic antioxidant comprises a copolymer of dicyclopentadiene with a mixture of 2- and 3-methyl phenols.

A copolymer of dicyclopentadiene with a mixture of 2- and 3-methyl phenols is sold by Lowi GmbH under the trade name "Lowinox 22CP46". It is believed to have the general formula



In the remainder of the specification this antioxidant is referred to as "22CP46".

We have discovered that this antioxidant has a combination of advantages which make it, so far as we are aware, one of only two commercially available antioxidants suitable for use in detergent powders containing nonionic surfactants, the other one being 'Topanol CA' (registered Trade Mark) which is a hindered phenol, the use of which is described in DOLS 2 806 702. It is stable in hot alkaline media and does not give rise to colouration in an otherwise colourless composition. It is soluble in nonionic surfactants of the sort most commonly used in detergent compositions, that is those having hydrophobes derived from C_8-20 primary and secondary alcohols and hydrophilic components formed from 5 to 20 moles of ethylene oxide. This solubility makes it extremely easy to handle in a factory environment. It is very heat stable and has low volatility, so it neither decomposes to unwanted decomposition products nor volatilises during a spray-drying process. It is very effective as an antioxidant at low levels and over a wide range of temperatures. Finally it appears to be physiologically and environmentally acceptable, unlike many other antioxidants.

We have examined a very large number of commercial antioxidants, but few have had such an impressive combination of advantages as 22CP46. Most conventional food antioxidants have poor stability, are volatile or produce colourations in detergent powders, either during manufacture or subsequently during storage. Many of the newer, more exotic antioxidants are also extremely suspect physiologically.

22CP46 can be used either simply mixed with a nonionic surfactant, to inhibit oxidation in a storage tank, or it can be admixed with the surfactant when the crutcher slurry is formulated to inhibit oxidation during spray-drying and subsequently.

22CP46 is extremely effective at very low levels in the detergent powder. As little as 0.001% based on the weight of the final detergent powder is effective, although 0.02 to 0.10% by weight is

preferred. Obviously the minimum effective amount will be used having regard to the cost of the material.

22CP46 is normally incorporated in the crutcher slurry in solution or dispersion but may also be injected into a high pressure line carrying pressurised slurry to the spraying nozzles of a spray-drying tower.

If nonionic surfactant is being supplied to the spray-drying tower in that way, then 22CP46 can be dissolved in the surfactant and injected at the same time.

The amount of nonionic surfactant present in the detergent slurry will be sufficient to provide from 2 to 50% by weight in the final powder. All of the nonionic surfactant required in the spray-dried powder may be incorporated into the slurry or part of it may be incorporated by another method, such as by spraying onto the spray-dried powder, or by using a preformed adjunct. In the latter case the slurry will contain 2 to 15% by weight of nonionic surfactant based on the final powder.

The invention is applicable not only to detergent slurries and powders in which the surfactant is nonionic, but also to those containing mixtures of nonionic surfactants with other surface active species. Examples of these are synthetic anionic detergents, primary and secondary alkyl sulphates, olefine sulphonates and alkyl benzene sulphonates, salts of fatty acids (soaps), cationic and zwitterionic surfactants.

As has been intimated, the invention is particularly applicable to the spray-drying of powders containing nonionic surfactants of the alkoxyated alcohol type although other nonionic surfactants which give powders susceptible to autoxidation will also exhibit the improvement.

The alcohols used can be primary or secondary alcohols containing straight or branched carbon chains. The number of carbon atoms will generally be from 6 to about 24, preferably from about 8 to 18 and most preferably from about 11 to 16. These alcohols may be the so-called synthetic alcohols made by the well-known Ziegler or Oxo processes, or the so-called "natural alcohols" made by hydrogenation of fatty acid derivatives, for example tallow alcohol.

The alkoxylation reaction will be carried out by conventional means, generally using ethylene oxide or propylene oxide or both. The degree of ethoxylation can vary widely both from one hydrophobe to the other and even when using a single hydrophobe. Thus, ethylene oxide chains containing as few as 1 and more than 20 ethylene oxide units are quite often found in nonionic surfactants and will be applicable here.

The choice of carbon chain length of the hydrophobe and the chain length of the hydrophobic alkoxy chain is largely determined by the detergent properties required of the molecule. The relationship between the chain length of the hydrophobic part of the molecule and that of the hydrophilic part can be expressed numerically as the hydrophilic-lipophilic balance (HLB). An approximate method of determining the HLB of alcohol ethoxylate is to use the expression

$$\text{HLB} = \frac{\text{Wt percentage of ethylene oxide}}{5}$$

Nonionic surfactants which are suitable for use in heavy duty fabric washing powders generally having an HLB in the range 9 to 16, although HLB's outside this range are not excluded.

An additional factor in the choice of nonionic surfactant is that the alcohols containing both short carbon and short ethoxylate chain lengths are relatively low boiling and can volatilise under the conditions prevailing in a spray-drying tower.

Preferred alcohol ethoxylates for use in this invention are derived from the following series:

Tergitols (Trade Mark) which are a series of ethoxylates of secondary alcohols sold by the Union Carbide Corporation, especially Tergitol 15-S-7, 15-S-9, 15-S-12 and 15-S-15 which are ethoxylates of a mixture of C_{11-15} alcohols and Tergitols 45-S-7, 45-S-9, 45-S-12 and 45-S-15 which are ethoxylates of a mixture of C_{14} and C_{15} alcohols, the degree of ethoxylation being shown by the postscript.

Ethoxylates of primary alcohols made by the Oxo process and containing about 20% of alpha branched material sold by Shell Chemicals Ltd and Shell Chemicals Inc as Dobanols and Neodols (Registered Trade Marks) respectively, especially Dobanol and Neodol 25-7, 25-9, 25-12 and 25-15 which are ethoxylates of a mixture of $C_{12}-C_{15}$ alcohols and Dobanol 45-7, 45-9, 45-12 and 45-15 which are ethoxylates of a mixture of C_{14-15} alcohols.

Ukanils (Trade Mark) which are a series of ethoxylates of Oxo alcohols containing about 25% of alpha methyl branched and about 10% of ethyl branched material (Acropols (Trade Mark) manufactured by Ugine Kuhlmann et Cie, especially Acropol 35-7, 35-9, 35-11 and 35-15 which are derived from a mixture of $C_{13}-C_{15}$ alcohols).

Synperonics (Trade Mark), a series of ethoxylates of alcohols containing 45-55% of alkyl branching, mostly methyl branching, sold by Imperial Chemical Industries Limited, especially those based on a C_{13-15} mixture of alcohols and ethoxylated to 7, 9, 11 and 15 units of ethylene oxide.

Ethoxylates of primary Ziegler alcohols (Alfols (Trade Mark) derived from ethylene, manufactured

by Conoco-Condea, especially Alfol 12/14-7, 12/14-9, 12/14-12, 12/14-15 and Alfol 14/12-7, 14/12-9, 14/12-12, 14/12-15 which are ethoxylates of mixtures of C_{12} and C_{14} alcohols.

Ethoxylates of primary Oxó alcohols containing about 60% branched material sometimes called Lials (Trade Mark) produced from olefins manufactured by Liquichimica.

5 Lutenols (Trade Mark), which are a series of ethoxylated alcohols sold by BASF, especially Lutensol A07 and Lutensol A08.

Lastly, ethoxylates of natural alcohols, such as tallow alcohol can be used.

The required HLB can be achieved not only by selecting the carbon chain length of the hydrophobe and the length of the ethyleneoxy chain in a single or substantially single material (because
10 of the nature of their process of production, all nonionic surfactants which are spoken of as if they were single substances are in fact mixtures). It can also be achieved by deliberately taking two "substances" of widely differing HLB's and mixing them. This approach is described in Netherlands patent application No. 7 413 522 and in Netherlands patent application No. 7 406 003. It is also possible to obtain the required HLB by "stripping" some chain lengths from a nonionic surfactant mixture as described in
15 patent applications based on US S/No. 453 462 and US patent 3 682 849.

The detergency builders which may be used in the compositions of this invention may be any of the sequestrant or precipitant builders which have been suggested to replace phosphate builders, or they may be phosphate salts, or mixtures of any one of these, generally in amounts from 10 to 60% by weight in the case of phosphate builders and 10 to 35% by weight in the case of non-phosphate ones.

20 Examples of detergency builders which may be used are ortho-, pyro- and tripolyphosphates; aluminosilicates; carbonates, especially the sodium carbonate/calcium carbonate combination; polyphosphonates such as ethane-1-hydroxy-1,1-diphosphonate; amine carboxylates such as nitrilotriacetates and ethylene diamine tetra acetates; ether carboxylates such as oxydiacetates, oxydisuccinates, carboxymethyloxysuccinates and malonates; citrates; mellitates; and salts of
25 polymeric carboxylic acids such as polymaleates, polyitaconates and polyacrylates. These salts will normally contain alkali metal or ammonium cations, preferably sodium.

Mixtures of sodium ortho- and tripolyphosphate are also suitable detergency builders, particularly mixtures in the range 10:1 to 1:5, preferably 5:1 to 1:1 tripolyphosphate to orthophosphate, in amounts of 10 to 60% by weight.

30 Other conventional components of detergent compositions may be present in conventional amounts. Examples of these include powder flow aids such as finely divided silicas and aluminosilicates, antiredeposition agents such as sodium carboxymethylcellulose, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, per-acid bleach precursors such as tetraacetylenediamine, chlorine-releasing bleaching agents such as trichloroisocyanuric acid and alkali
35 metal salts of dichloroisocyanuric acid, fabric softening agents such as clays of the smectite and illite types, antiashing aids, starches, slurry stabilisers such as copolyethylene maleic anhydride and copolyvinylmethylether maleic anhydride, usually in salt form, inorganic salts such as sodium silicates and sodium sulphate, and usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants. The detergent compositions usually have
40 an alkaline pH, generally in the region of pH 9—11, which is achieved by the presence of alkaline salts, especially sodium silicates such as the meta-, neutral or alkaline silicates ($Na_2O:SiO_2$ 1:1 to 1:3.3), preferably at levels up to about 15% by weight.

The invention will be illustrated by means of the following Examples.

45 Example 1

In this Example the effectiveness of 22CP46 in inhibiting oxidation is demonstrated by a modification of the method of P. L. Bowes and A. Cameron described in J. Appl. Chem. & Biotechnol. 1971. This method involves suspending a cubic, open-topped basket (side length 10 cm) containing the powder under test in an oven set to a given temperature. The powder has a thermocouple
50 embedded in the centre of it, connected to a chart recorder. When spontaneous combustion sets in, a rapid rise in temperature occurs. The time taken for this rapid rise in temperature is recorded. Results can be presented either as the time taken to autoxidise at a given temperature (times greater than 24 hours for samples held at 150°C are considered good), or as the maximum temperature at which no oxidation occurs within 24 hours (temperature increments of 10°C are normally used when ease of
55 autoxidation is assessed in this way).

The powder formulations and the maximum temperatures at which no autoxidation occurs within 24 hours are shown below.

60

65

% by weight

Ingredient		A	B	C	D	E	F
5	C ₁₂₋₁₅ primary alcohol 7EO ethoxylate	11.9	11.9	11.9	18.9	13.5	13.5
	Tallow ethanalamide	2.2	2.2	2.2	2.2	2.0	2.0
	Tallow soap	1.5	1.5	1.5	1.5	1.3	1.3
	Alkaline sodium silicate (2:1 ratio)	14.8	14.8	14.8	14.8	13.3	13.3
	Sodium tripolyphosphate	48.4	48.4	48.4	48.4	43.3	43.3
10	Sodium sulphate	5.4	5.4	5.4	5.4	11.8	11.8
	22CP46	Nil	0.015	0.035	0.74	Nil	0.13
	Moisture and minor ingredients	to 100	to 100	to 100	to 100	to 100	to 100
	Maximum temperature at which autoxidation did not occur (°C)	130	150	160	160	130	200

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The 22CP46 imparted no colouration to the spray-dried material in the spray-drying power exhaust gases, thus confirming its stability to both alkaline media and heat, and its low volatility.

20 Example 2

This Example shows the heat stabilising effects of two further antioxidants. However, whereas incorporation of 22CP46 resulted in normal white powders, use of these antioxidants resulted in coloured powders, because of the instability of the antioxidants in alkaline media.

25

% by weight

Ingredient		G	H	I
30	C ₁₂₋₁₅ secondary alcohol 9EO ethoxylate	16.2	16.2	16.2
	Coconut ethanalamide	2.2	2.2	2.2
	Coconut soap	3.0	3.0	3.0
	Alkaline sodium silicate	7.6	7.6	7.6
	Sodium tripolyphosphate	54.8	54.8	54.8
35	Sodium toluene sulphonate	1.5	1.5	1.5
	Gum Guaicum ^(a)	0.15	Nil	Nil
	Butyl hydroxyanisole	Nil	0.15	Nil
	Water and minor ingredients	to 100	to 100	to 100
	Time to autoxidation at 150°C (hours)	15	11	8
40	Colour of spray dried powder	cream/ yellow	pink	white

(a) Gum Guaicum is an antioxidant of the hindered phenol type used in foodstuffs.

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Claims

1. A composition comprising from 2 to 50% by weight of a nonionic surfactant in the form of a C₆—C₂₄ primary or secondary alcohol ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol and from 0.001 to 0.5% by weight of a phenolic antioxidant, characterised in that the phenolic antioxidant comprises a copolymer of dicyclopentadiene with a mixture of 2- and 3-methyl phenols.
2. A composition according to claim 1 in the form of a spray-dried detergent powder.
3. A composition according to claim 1 or claim 2 comprising from 0.02 to 0.10% by weight of the copolymer.
4. A detergent composition according to any one of the preceding claims comprising from 10 to 60% by weight of a phosphate detergency builder.
5. A detergent composition according to claim 4 comprising from 10 to 35% by weight of a non-phosphate detergency builder.
6. A process for the manufacture of a detergent powder which comprises forming an aqueous slurry comprising an amount of a nonionic surfactant in the form of a C₆—C₂₄ primary or secondary alcohol ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol sufficient to provide from 2 to 50% by weight of the surfactant in the spray-dried powder and a minor amount of a phenolic antioxidant, and spray-drying it characterised in that the phenolic antioxidant comprises a copolymer of dicyclopentadiene with a mixture of 2- and 3-methyl phenols.

Revendications

1. Composition contenant de 2 à 50% en poids d'un agent tensio-actif non-ionique sous la forme d'un alcool primaire ou secondaire en C_6 à C_{24} éthoxylé avec de 3 à 25 moles d'éthylénoxyde par mole d'alcool et de 0,001 à 0,5% en poids d'un anti-oxydant phénolique, caractérisée en ce que l'anti-oxydant phénolique comprend un copolymère de dicyclopentadiène avec un mélange de 2- et 3-méthylphénols.
2. Composition selon la revendication 1 sous la forme d'une poudre détergente séchée par pulvérisation.
3. Composition selon la revendication 1 ou la revendication 2 comprenant de 0,02 à 0,10% en poids du copolymère.
4. Composition détergente selon l'une quelconque des revendications précédentes comprenant de 10 à 60% en poids d'un auxiliaire de détergence phosphaté.
5. Composition détergente selon la revendication 4 comprenant de 10 à 35% en poids d'un auxiliaire de détergence non phosphaté.
6. Procédé de préparation d'une poudre détergente dans lequel on forme une bouillie aqueuse comprenant une certaine quantité d'un agent tension-actif non-ionique sous la forme d'un alcool primaire ou secondaire en C_6 à C_{24} éthoxylé avec de 3 à 25 moles d'éthylénoxyde par mole d'alcool de manière suffisante pour fournir de 2 à 50% en poids de l'agent tensio-actif dans la poudre séchée par pulvérisation et une quantité secondaire d'un anti-oxydant phénolique, et on la sèche par pulvérisation, caractérisé en ce que l'anti-oxydant phénolique comprend un copolymère de dicyclopentadiène avec un mélange de 2- et 3-méthyl-phénols.

Patentansprüche

1. Mittel mit 2 bis 50 Gew.-% eines nicht-ionischen Tensids in Form eines C_6 — C_{24} -prim.- oder -sec.-Alkohols, ethoxyliert mit 3 bis 25 Mol Ethylenoxid pro Mol Alkohol, und 0,001 bis 0,5 Gew.-% eines phenolischen Antioxidans, dadurch gekennzeichnet, daß das phenolische Antioxidans ein Copolymer von Dicyclopentadien mit einem Gemisch von 2- und 3-Methylphenol umfaßt.
2. Mittel nach Anspruch 1 in Form eines sprühgetrockneten Reinigungspulvers.
3. Mittel nach Anspruch 1 oder 2 mit 0,02 bis 0,10 Gew.-% des Copolymeren.
4. Reinigungsmittel nach irgendeinem der vorhergehenden Ansprüche mit 10 bis 60 Gew.-% eines Phosphat-Waschmittel-Builders.
5. Reinigungsmittel nach Anspruch 4 mit 10 bis 35 Gew.-% eines Nicht-Phosphat-Waschmittelbuilders.
6. Verfahren zur Herstellung eines Reinigungsmittel pulvers, das die Bildung eines wäßrigen Breis mit einer Menge eines nicht-ionischen Tensids in Form eines C_6 — C_{24} -prim.-oder-sec.-Alkohols, ethoxyliert mit 3 bis 25 Mol Ethylenoxid pro Mol Alkohol, ausreichend, um 2 bis 50 Gew.-% des Tensids im sprühgetrockneten Pulver zu liefern, und einer Mindermenge eines phenolischen Antioxidans und Sprühtrocknen umfaßt, dadurch gekennzeichnet, daß das phenolische Antioxidans ein Copolymer von Dicyclopentadien mit einem Gemisch von 2- und 3-Methylphenol umfaßt.