



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 157 483
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **85301075.9**

(51) Int. Cl.⁴: **C 11 D 3/39, D 06 L 3/02**

(22) Date of filing: **19.02.85**

(30) Priority: **28.02.84 GB 8405189**

(71) Applicant: **Interox Chemicals Limited, Hanover House 14 Hanover Square, London W1R 0BE (GB)**

(43) Date of publication of application: **09.10.85**
Bulletin 85/41

(72) Inventor: **Leaver, John Philip, Rowton Grange West, Whitchurch Road Rowton Chester (GB)**
Inventor: **MacKirdy, Iain Stewart, 11, Pythian Crescent, Penketh Warrington, WA5 2BT Cheshire (GB)**
Inventor: **Sanderson, William Ronald, 23, Rossall Road, Great Sankey Warrington WA5 2SP Cheshire (GB)**

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI NL SE**

(74) Representative: **Pearce, Timothy et al, Laporte Industries Limited Group Patent Department P.O. Box 2 Moorfield Road, Widnes Cheshire WA8 0JU (GB)**

(54) **Peroxide activation.**

(57) Hydrogen peroxide and persalts are markedly less efficient bleaching agents at hand-hot temperatures than near the boiling point of solutions containing them.

In order to improve the bleaching performance of such percompounds, the invention provides an activator system comprising a catalytic amount of a soluble manganous salt in conjunction with an excess amount of an alkali metal citrate or citric acid. Typically about 0.5 to 5 mg/l manganous ion is provided in solution together with 100 to 5000 mg/l citrate, and percompound providing from 35 to 10000 ppm mg/l available oxygen.

The bleach system can be employed on its own, or as an additive to a washing composition or even as a component of the latter.

EP 0 157 483 A1

Peroxide Activation

The present invention relates to peroxide activation and in particular to the activation of compositions containing hydrogen peroxide or persalts which generate hydrogen peroxide under the conditions of use.

Conventionally, one class of bleaching agents comprises hydrogen peroxide and persalts that generate it in use conditions. Such bleaching agents are comparatively ineffective at stain removal from fabrics or hard surfaces at low washing temperatures, such as ambient to 60°C. Accordingly, and especially in the wake of increased energy prices, considerable efforts have been devoted to activating the bleaching agents at those temperatures.

One class of activators which have received intermittent attention comprise transition metals. It has long been recognised that first row transition metals such as iron or copper catalyse peroxide decomposition, but harnessing the reaction between the two components to enhance low temperature stain removal has proven to be rather elusive. The teaching provided by the prior art in some respects appears to be self-conflicting and in other aspects the generalised statements appear to be unwarranted by the experimental support.

One transition metal that appears to be capable of activating hydrogen peroxide or persalts is manganese. Passing reference is made to it in US-A-3156654, but the patent asserts that it must be used in conjunction with chelating agents which meet certain criteria of which most

examples fall under the heading aminocarboxylic acids. When the process was tested using a representative aminocarboxylate and hydrogen peroxide under buffered alkaline conditions, the system with a catalytic amount of manganese sulphate bleached no better than hydrogen peroxide alone at the same conditions. Clearly US-A-3156654 represented mere speculation in so far as it referred to manganese.

US-A-3532634 also described compositions containing a transition metal and a persalt, but they demonstrated activation only in the presence of a range of weakly chelating agents, different from those in US-A-3156654 when an organic persalt activator was present as well. Stronger chelating agents such as aminocarboxylic acids were specifically excluded. In a comparative example no activation was apparent when manganous sulphate and picolinic acid was employed with a heavy duty detergent composition to which sodium perborate had been added.

In more recent times EP-A-72166 describes a multi-component activator system for persalts including two metal catalysts and a range of sequestrants of which one major specified class comprises amino(poly)carboxylates. It will be recognised that these sequestrants are the same as those referred to in US-A-3156654 and those specifically excluded from US-A-3532634. Consequently this specification provides no direct teaching upon the provision of a single metal catalyst system, when similar comments apply as for the repeat test described in the passage relating to US-A-3156654.

Most recently, in EP-A-82563, there is described activation of a persalt by manganese but it demands the presence of a carbonate. In practice, fabrics typically are stained with a variety of different types of stains, including clay or grease stains which respond relatively poorly to cleansing compositions built with carbonate and presumably in recognition of such practical matters the specification includes a list of inorganic and organic

complexing builders for use in conjunction with carbonate. Indeed, all their Examples include one or more auxiliary builders. However the Examples and particularly Examples I, III and XII show clearly the deleterious effect of substituting at least part of the carbonate by their main auxiliary detergent builder, namely sodium tripolyphosphate. It is thus a reasonable inference from EP-A-82563 that the key to employing manganese as a persalt promoter rests with the use of carbonate and the other builders retard or obstruct that effect. This is fully consistent with experimental observations that inorganic builders such as tripolyphosphates and organic complexing builders such as aminocarboxylates as sole builder complex the manganese such that no activation of persalts is noticeable.

Surprisingly, it has now been found that not all organic complexing builders exhibit the same deleterious effect upon manganese activation of persalts.

According to the present invention there is provided a process for activating hydrogen peroxide in which hydrogen peroxide or a persalt that generates hydrogen peroxide is brought into contact with a catalytic amount of a manganous salt in the presence of a substantial excess of an organic complexing builder selected from alkali metal citrates and citric acid.

The manganese used in the present invention can be derived from any manganese (II) salt, such as manganous sulphate and manganous chloride, or from any manganese compound or substrate which delivers manganese (II) ions in aqueous solution. The substrate can comprise an absorbent particulate or non particulate substrate which previously has absorbed a manganous salt. Non particulate substrates include fibres, foams, sponges and films often made from certain cellulose ethers, alginates, polyvinyl alcohols or polyvinyl pyrrolidene polymers. Particulate substrates include clays, including bentonites, and any of the general classes of zeolites that hitherto have been proposed for incorporation in washing compositions, in for example

FR-A-2225568, DE-A-2422655 or BE-A-849382, which include manganous exchanged zeolites A, X and Y.

5 The effect of increasing the concentration of soluble manganese salt in the washing solution first results in enhanced activation of hydrogen peroxide and further increase then results in a progressive reduction in the enhancement, possibly even in impairment of stain bleaching performance. Thus, the amount of manganous salt to employ represents a balance between enhanced activation of hydrogen
10 peroxide and the deleterious effect possibly resulting from an increased propensity to deposit an insoluble salt upon the surface being bleached. Expressed in terms of the weight of manganous ion, it is desirable for a bleaching solution to contain at least 0.5 mg/l and typically not more
15 than 10 mg/l available for complexing with the citrate or citric acid. Use of amounts of available manganese above the upper specified amount tend towards impaired bleaching. In practice, it is often convenient to select the available manganous concentration within the range of 1 to 5 mg/l.

20 The concentration of the citrate/citric acid is desirably at least 10 times that of the manganous ion, and in particular at least 100 mg/l. It is convenient, often, to select the citrate/citric acid concentration in the range of 100 to 5000 mg/l since such a concentration range can
25 readily be obtained by dissolution of citrate/citric acid built washing composition in the washing/bleaching bath at recommended dosages.

The washing/bleaching bath also contains hydrogen peroxide at a concentration sufficient to provide normally
30 at least 5 and preferably at least 20 mg/l available oxygen (avox) in solution. For stain removal in domestic washing processes the avox is frequently selected in the range of 35 to 200 mg/l avox, for combined stain removal and disinfection often from 200 to 500 mg/l avox and for textile
35 bleaching often from 1000 to 10,000 mg/l avox. The hydrogen peroxide can be added as such or introduced as any persalt including alkali metal perborates, especially sodium

perborate tetrahydrate, trihydrate or monohydrate, urea peroxide, or as an adduct with sodium sulphate and sodium or potassium chloride. The presence of carbonate can be tolerated within the system according to the invention and thus sodium percarbonate may be employed.

For effective washing/bleaching of stains, it is especially desirable to produce alkaline conditions particularly from about pH 8 to about pH 10.5, and for textile bleaching especially from about pH 10 to about pH 12-13. This can be achieved either by introduction of an alkali such as sodium hydroxide under automatic or manual control as is feasible within commercial laundry or industrial textile bleaching operations, or more conveniently in domestic washing/bleaching operations by the presence of an alkaline buffer or buffer combination. It will be recognised that both the persalts and the citrate builder (especially when added as trisodium citrate) enable the washing solution to reach an alkaline pH automatically.

The aforementioned components can be added individually in controlled doses to the solution, or more conveniently where the components have a compatible physical form, two or more of them can be formulated in the precalculated proportions to yield the desired concentration of each in use. For domestic use it is easiest to employ particulate mixtures. Accordingly, in a further aspect of the present invention there is provided a particulate activator composition comprising at least 0.5 and preferably 1-5 parts by weight of a manganous salt, calculated on the basis of the weight of the manganous ion part thereof, and from 100 to 5000, preferably 250 to 2000 parts by weight of the citric acid/alkali metal citrate complexing builder. Such a formulation can be provided as such or be aggregated to form tablets, granulates, pills or the like thereby permitting the unitary dosing of precalculated quantity of each component to a hydrogen peroxide solution.

In a yet further aspect of the present invention, there is incorporated with the aforementioned activator

composition from 200 to 4000, preferably 500 to 2000 parts by weight of a persalt, thereby forming a bleach composition that can be employed by itself or as an adjuvant with a surfactant composition, particularly an unbuild composition or alternatively as a component in a surfactant washing composition.

Thus, washing compositions according to the present invention comprise a bleaching composition as outlined hereinabove in a weight amount of at least 5% and generally from 10 to 60%, especially 15 to 50% of the composition, a surfactant, in a weight amount of at least 2% to 70% and generally 5 to 50%, processing acids in a weight of 0 to 40%, and other detergent adjuvants in a total amount of 0 to 20%.

The surfactants that can be employed in the present invention include anionic, nonionic, zwitterionic or cationic surfactants or mixtures thereof, which are suitable for incorporation in persalt-containing washing compositions. In practice they are selected to exhibit water solubility.

The anionic surfactants are normally alkali metal or ammonium salts, especially sodium, though a proportion of alkaline earth metal salts can be tolerated. One or more anionic surfactants are often selected from linear alkyl benzene sulphonates, especially having C₉-C₁₅ in the alkyl chain, alkyl sulphates, particularly C₁₀-C₂₂, olefin sulphonates, particularly C₁₀-C₂₄, alkane and/or hydroxyalkane sulphonates, often C₁₀-C₂₄, alkyl phenoxy ether sulphates, often with C₈-C₁₂ alkyl chain and 1-10 ethylene oxide units, alkyl ether sulphates often with C₁₀-C₂₀ alkyl chain and 1-10, preferably 2-4 ethylene oxide units and soaps, particularly C₁₂-C₂₀. Various other anionic surfactants often provide at least part of the total added including sulphocarboxylates, alkyl glyceryl ether sulphonates, monoglyceride sulphates and sulphonates, and phosphated ethylene oxide-based nonionic surfactants.

The nonionic surfactants for incorporation in invention

washing compositions generally comprise condensation products of ethylene oxide and propylene oxide, typically 5-30 units, with an aliphatic or aromatic alcohol or an aliphatic acid amine or amide. In such nonionic

5 surfactants, the hydrophobic aliphatic moiety often has a chain length of C₈-C₂₂; and is C₆-C₁₂ when present in an alkyl aromatic group. Other usable nonionic surfactants are condensates of glycerol and sorbitol.

10 It is convenient, usually to employ both an anionic surfactant component and a nonionic surfactant component in washing compositions, in a weight ratio often from 10:1 to 1:10.

Semipolar surfactants are useable herein and include water-soluble amine oxides, phosphine oxides and sulphur
15 oxides, each containing a C₁₀-C₂₂ alkyl chain and often 2 C₁-C₃ alkyl chains.

Zwitterionic surfactants herein are often selected from water-soluble derivatives of aliphatic quaternary ammonium, phosphonium and sulphonium cationic compounds in which the
20 aliphatic moieties are straight or branched, and in which one substituent is C₈-C₁₈ and one terminates in an anionic water-solubilizing group, especially a sulphonate group for example alkyl-hydroxy-propane-sulphonates and alkyl-dimethyl-ammonio-hydroxy- propane-sulphonates.

25 The cationic surface active agents when employed are often selected from quaternary ammonium compounds having one or two C₈-C₂₀ straight or branched hydrophobic groups, e.g. cetyl trimethyl ammonium bromide or chloride, dioctadecyl dimethyl ammonium chloride, and the fatty alkyl amines.

30 It will be understood that various commonly used detergent builders including polyphosphates and amino carboxylic acid complexing builders have been shown to prevent manganese catalysing hydrogen peroxide bleaching of stains under conditions identical to those in which citrate
35 enables the manganese to activate. The presence of such auxiliary builders tends to reduce the citrate/manganese/hydrogen peroxide activation, to an

increasing extent as the manganese complexes with the auxiliary builder. Despite that, in practice it is desirable to take into account the other functions that such builders perform and a balance is struck between the possible benefits of adding them, such as improved sequestration of calcium and magnesium ions, or improved synergism with anionic surfactants especially alkyl benzene sulphonates and the somewhat impaired removal of bleachable stains. Accordingly, washing compositions and processes of the present invention tolerate the presence of auxiliary builders selected from both water soluble or insoluble particulate builders. Such builders can include alkali metal polyphosphates, pyrophosphates, polymetaphosphates and alkali metal silicates as well as zeolites obeying the general formula $(M_2O)_x.(Al_2O_3).(SiO_3)_y$ in which M is a monovalent metal especially sodium, x is 0.7 to 1.5 and y is 1.3 to 4.0, including zeolites A and X and mixtures thereof. Auxiliary organic builders include nitrilotracetic acid, sodium salt and related amino carboxylic acid salts. The amount of auxiliary builder present depends upon the extent to which the user is willing to tolerate impaired performance in bleachable stains. As a guide it is preferable for the weight of auxiliary builder to be less than the weight of citrate, lest some benefit is still retained even when the proportion of citrate falls to as low as 20% of the total builder weight. In practice this means that it is normally selected in the range of 0-30%, and often represents 5-20% of the total formulation. Indeed, in view of the quality of citrate as builder in its own right, the addition of such auxiliary builders is not necessary, and their inclusion may be primarily at low levels of e.g. up to 5-10% for other functions such as pH control etc, rather than for the normal function of overcoming hardness.

The processing aid, when present, is usually selected from sodium and/or magnesium sulphate.

The detergent auxiliary agents present are normally selected from soil antiredeposition agents, dye transfer

inhibitors, optical brightening agents, peroxy stabilisers, corrosion inhibitors, bactericides, foam enhancers, foam inhibitors, thickeners, absorbents, abrasives, diluents, dyes, perfumes and proteolytic enzymes. Amongst the auxiliary agents, carboxymethyl cellulose salts and polyvinylpyrrolidines deserve mention as SARDs, the various aminocarboxylates, aminomethylenephosphonates, hydroxy quinolines and dipicolinic acid as peroxy stabilisers and/or dye transfer inhibitors, silicates for corrosion inhibition, quaternary ammonium or pyridinium halides as bactericides, alkanolamides and ethylene oxide/propylene oxide copolymers to regulate foaming. Derivatives of diaminostilbene sulphonic acid, diarylpyrazolines and aminocoumarins are examples of OBA's, anhydrous sodium or magnesium sulphate are examples of absorbents and diluents, silica or maleic modified cellulose, polyethylene oxide, e.g. above MW of 10,000, maleic anhydride copolymers with ethylene, styrene or methylvinyl ether, especially above 50,000 MW, or polyvinyl pyrrolidine as a thickener, and silica or kieselguhr as abrasives. Naturally, it is preferred to select dyes and perfumes known not to interact readily with peroxygen compounds, and to coat any enzyme with water soluble/dispersible coating for storage protection.

The processes for washing articles according to the present invention can be carried out at a temperature from ambient temperature up to the boiling point of the washing solution. Compositions according to the present invention are particularly well suited to a process at which washing or bleaching is carried out by steeping at ambient or by heating the solution to a temperature from about 25° to 60°. Alternatively the washing and bleaching processes may be effected by heating up a cold washing solution. A combination of processes can be used, such as cold steeping followed by a wash at 30, 40 or 50°C.

In general, the rate of removal of stains is enhanced by employing a higher temperature and by higher Avox. concentrations, but by virtue of the rate at which the

invention washing compositions dissolve or are dispersed in the wash solution, the contact period between solution and fabric can conveniently be as short as 5 minutes. Longer periods of for example typically 10 to 30 minutes and up to 1 hour tend to provide greater soil removal. In cold washing or steeping even longer periods can be employed, such as steeping overnight.

Having described the invention in general terms, specific demonstrations of the effectiveness of the invention are given by way of example only.

Example 1 and comparisons 2-5

In each of these Examples and comparisons swatches of red wine stained cotton limbric cloth were washed for 20 minutes in an aqueous alkaline solution formed by dissolving hydrogen peroxide (0.375 g/l) manganous sulphate tetrahydrate (8 mg/l, providing 2 mg/l Mn^{2+}) and builder in water buffered to pH 10.1 with sodium hydroxide, and which contained 250 mg/l hardness in a Ca:Mg weight ratio of 3:1. The washing trials were carried out at 40°C in a laboratory scale washing machine available from the US Testing Corporation, under the trademark TERGOTOMETER. After each swatch had been washed, it was rinsed with cold water, air dried and its reflectance (R_w) measured using an Instrumental Colour System MICROMATCH reflectance spectrophotometer equipped with a xenon lamp, light source filtered to approximate to daylight. The reflectance was compared with the original unstained cloth (R_u) and the stained cloth (R_s) and the percentage stain removal calculated using the formula

$$\% \text{ stain removal} = 100 \times (R_w - R_u) / (R_s - R_u)$$

The stain removal gain shown is the difference attributable to adding the builder manganese to the bleach solution.

The results are summarised in Table 1.

Table 1

	Builder	Mn Salt	Stain Removal	
			%	% gain
5	Ex 1 trisodium citrate (1 gpl)	+	67	21
	C2 -	-	46	ref
	C3 trisodium nitrilo- triacetate (1 gpl)	+	47	1
10	C4 trisodium ortho- phosphate (1 gpl)	+	49	3
	C5 sodium carbonate (0.78 gpl)	+	57	11

From Table 1, it can be seen that neither of the two well known classes of builders, namely the aminocarboxylate salts and the phosphate salts allowed manganese to catalyse hydrogen peroxide stain removal in alkaline conditions and secondly that even though sodium carbonate did demonstrate some gain in stain removal, sodium citrate gained nearly twice as much at only half the molar concentration.

The activator composition corresponding to the process in Example 1 comprise 8 parts by weight manganese sulphate tetrahydrate per 1000 parts by weight of trisodium citrate. Examples 6 and 7 and Comparisons 8, 9, 10

The washing procedure and testing of Example 1 was repeated except that the washing solutions were allowed to attain their natural pH and the peroxide in solution was provided by sodium perborate tetrahydrate added at 1.15 g/l and in Example 7 and Comparison 10, 4 times the weight of manganous salt was added.

The results are summarised in Table 2

Table 2

	Builder	Mn Salt	pH	Stain Removal	
				%	% gain/loss
Ex 6	+	+	9.8	51	16
5 Ex 7	+	4+	9.8	39	4
Comp 8	-	-	9.4	35	ref
Comp 9	-	+	9.4	31	-4
Comp 10	-	4+	9.4	4	-31

From Table 2 it can be seen that the effect of
10 introducing the active oxygen in the form of sodium
perborate would normally depress the stain removal but by
adding sodium citrate as well, a substantial gain in stain
removal can be achieved. However, the practical benefit
tends to diminish as the concentration of manganous salt
15 increases beyond its optimum, though the gain over the same
solution but in the absence of citrate remains extremely
marked.

The bleach composition corresponding to the Example 6
or 7 processes comprises 8 respectfully or 32 parts by
20 weight manganese sulphate tetrahydrate, 1000 parts by weight
trisodium citrate and 1150 parts by weight sodium perborate
tetrahydrate.

Example 11 and Comparison 12

In this Example and Comparison, washing solutions
25 according to Example 6 and Comparison 8 were made, but
employing additionally a phosphate-free detergent
composition called US Tide (Trademark) at a concentration of
6 g/l having a composition analysed as approximately

linear alkyl (av C11.5) benzene sulphonate (sodium
30 salt) 12.5%, nonionic ethoxylated surfactant 2.6%, zeolite A
(sodium) 30%, sodium sulphate 27%, sodium carbonate 20%,
phosphate 0.3%, carboxymethyl cellulose, OBA and other
detergent adjuncts 1% and the balance water. The conditions
of washing and testing further samples of the same swatches
35 were exactly the same as in Example 1.

In Example 11, there was a stain removal of 49% whereas
in Comparison 12 the stain removal was only 41%. This

indicates that it is beneficial to employ a manganous salt
in the presence of trisodium citrate and sodium perborate in
the presence of a substantial concentration of a detergent
composition, which provides auxiliary builders and
5 surfactants.

The Examples herein show clearly the advantage of
employing citrate as builder for manganese activated
persalat/H₂O₂ bleaching in comparison with several other
commonly used builders. They were carried out in
10 calcium-containing hard water. The use of calcium and
certain other alkaline earth metals to promote manganese
activation is the subject of an application of even date.

15

20

25

30

35

CLAIMS:-

1. A process for activating hydrogen peroxide in which hydrogen peroxide or a persalt that generates hydrogen peroxide is brought into contact with a catalytic amount of a manganous salt in the presence of a substantial excess of an organic complexing builder characterised in that the organic complexing builder is selected from alkali metal citrates and citric acid.
2. A process according to claim 1 characterised in that the concentration of manganous ion in solution is from 0.5 to 10 mg/l.
3. A process according to claim 2 characterised in that the concentration of manganous ion in solution is from 1 to 5 mg/l.
4. A process according to any preceding claim characterised in that the ion concentration of citrate/citric acid in solution is at least 10 times that of the manganous ion.
5. A process according to claim 4 characterised in that the concentration of citrate/citric acid in solution is from 100 to 5000 mg/l.
6. A process according to any preceding claim characterised in that the hydrogen peroxide added as such or in the form of a persalt provides a concentration of at least 20 mg/l available oxygen (avox) in solution.
7. A process according to claim 6 characterised in that the avox is from 35 to 200 mg/l for stain removal.

8. A process according to any preceding claim characterised in that the bleaching solution has a pH of from pH 8 to pH 10.5.
9. A process according to any preceding claim which is carried out at ambient to 60°C or commences within that range.
10. An activator composition comprising a manganese salt and a builder characterised in that it contains from 0.5 to 5 parts by weight of a manganous ion salt calculated as the weight of the manganous ion and from 100 to 5000 parts by weight of an alkali metal citrate and/or citric acid.
11. A composition according to claim 10 characterised in that it comprises from 1 to 5 parts manganous salt and from 250 to 2000 parts of alkali metal citrate and/or citric acid.
12. A bleach composition comprising a persalt and an activator characterised in that it comprises the activator composition according to either of claims 10 or 11 together with 200 to 4000 parts by weight of a persalt.
13. A bleach composition according to claim 12 characterised in that it contains 500 to 2000 parts of the persalt.
14. A washing composition comprising a surfactant and a bleach characterised in that it contains at least 5% w/w of the bleach composition according to claim 12 or 13, from 2 to 70% w/w of one or more surfactants, from 0 to 40% w/w of processing aids, and from 0 to 20% w/w of detergent adjuvants.

15. A composition according to claim 14 characterised in that it contains additionally from 0 to 30% w/w of an auxiliary builder.
16. A composition according to claim 14 or 15 characterised in that it contains from 15 to 50% of the bleaching composition, and from 5 to 50% surfactant.
17. A process or composition according to any preceding claim characterised in that trisodium citrate is employed as the complexing builder.
18. A process or composition according to any preceding claim characterised in that the persalt is sodium perborate tetrahydrate or monohydrate.
19. Any process for the activation of hydrogen peroxide or a persalt, or any activation composition or bleach composition or washing composition including one or more novel features substantially as described herein or novel combination of features substantially as described herein.



European Patent
Office

EUROPEAN SEARCH REPORT

0157483

Application number

EP 85 30 1075

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	EP-A-0 072 166 (PROCTER & GAMBLE CO.) * Claims 1,2 *		C 11 D 3/39 D 06 L 3/02
D,A	US-A-3 532 634 (W.G. WOODS) * Claims 1,10 *		
P,A	EP-A-0 111 964 (UNILEVER NV) * Claims 1-5 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 D 3/00 D 06 L 3/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 21-05-1985	Examiner SCHULTZE D
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	