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(54) **Synergistic liquid composition and use of the same for removing substances strongly bound to surfaces**

(57) The invention relates to a liquid composition having synergistic dissolving effect, comprising  
a) at least one alkylene glycol ether of the general formula  $(C_3-C_6\text{-alkyl})-(O-CH_2-CH_2)_n-OH$ , where the value of  $n$  is 1 to 5,  
b) at least one surfactant and  
c) water,  
where the mass ratio of component a) to component b)

ranges from 4:1 to 80:1.

The liquid composition of the invention is useful for cleaning smooth or porous surfaces, for example ceramic, plastered wall, granite, lime stone, cast stone or concrete, contaminated with dyestuff, heavy oil and/or bitumen.

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**Description****Field of the invention**

5 [0001] The present invention relates to a liquid composition having synergistic dissolving effect and use of the same to remove pollutants strongly bound to surfaces.

**Background of the invention**

10 [0002] It is known that various organic solvents (alcohols, ketones, aromatic liquids), either alone or as solvent mixtures, may be applied to different surfaces to remove strongly bound pollutants, such as dyestuff, oily substances, bitumen and so forth. The different organic solvents per se have extremely good dissolving effect, however, their serious detrimental effect on health and environment is a disadvantage.

15 [0003] It is likewise known that micellar-structure aqueous solutions of surface active agents (surfactants) may be applied to clean different surfaces. The solubility of substances otherwise immiscible with water or only sparingly miscible with water (hydrocarbons for example) increases if the same are added to micellar solutions, since the oleophilic components get solubilized in the core of the micelles. If the surfactant concentration is considerably higher than cmc (critical micellization concentration) and the micellar system contains an additional auxiliary surfactant (for example an aliphatic alcohol of medium chain length such as n-butanol, n-pentanol and so forth), then further addition of the organic component leads to conversion of the swollen micellar system into an oil-in-water (o/w) type microemulsion.

20 [0004] Combined concentration of the surfactant and the auxiliary surfactant (co-surfactant) at the observed point of microemulsion formation is called the critical microemulsion concentration [1-5].

25 [0005] Thus, microemulsions, being molecularly heterogeneous systems with nanostructured discontinuities, form spontaneously from a polar liquid (generally water), an immiscible apolar liquid and some type of surfactant (anionic, cationic or non-ionic), without an input of energy.

[0006] In addition to the above mentioned "normal micellar" o/w type emulsions, "reverse micellar" w/o type colloidal systems exist as well. Inverse micelles may form in the presence or absence of water, but in the latter case the cmc is not well defined and the systems are highly polydisperse. By adding water, i.e. changing the H<sub>2</sub>O/surfactant molar ratio, the size and shape of the forming micelles can be affected and regulated fairly arbitrarily [6,7].

30 [0007] It has so far been proven in practice that aqueous micellar solutions are unable to remove bound dyestuff from surfaces, but at the best, these are applicable only to clean oily or greasy surfaces. Microemulsions are excellent cleaning supplies and can be suitable to dissolve even surface bound (sun-dried) dyestuff in some cases. However, microemulsions imply considerable environmental load since they contain aromatic or aliphatic hydrocarbons in an amount up to 10-20% which contaminate the environment during application, thus, their use is limited.

**Object of the invention**

[0008] Because of the drawbacks of microemulsions, it was desirable to provide a novel liquid composition which is environmentally sound in its constitution and possesses good dissolving capacity at the same time.

40 [0009] The object of the invention was attained by providing a liquid composition having synergistic dissolving effect, which comprises

- a) at least one alkylene glycol ether of general formula (C<sub>3</sub>-C<sub>6</sub>-alkyl)-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-OH, where the value of n is 1 to 5,
- b) at least one surfactant and
- 45 c) water,

where the mass ratio of component a) to component b) ranges from 4:1 to 80:1.

[0010] The liquid composition of the invention can be used for cleaning surfaces contaminated with dyestuff, heavy oil and/or bitumen.

**Brief description of the drawings**

[0011] In

55 Figure 1 the relative excess dissolving capacity or rather the synergistic dissolving effect of five liquid compositions of the invention (compositions Nos. 1 to 5) are compared graphically.

Figures 2.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the AOT and butyl diglycol contents, respectively.

Figures 3.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the DAM and butyl diglycol contents, respectively, at the same concentration (0.5 % by mass) of AOT.

Figures 4.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the DAM and butyl diglycol contents, respectively, at the same concentration (1.0 % by mass) of AOT.

Figures 5.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the DAM and butyl diglycol contents, respectively, at the same concentration (1.5 % by mass) of AOT.

Figures 6.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the Lutensol\*GD70 and butyl diglycol contents, respectively.

Figures 7.a-b show the dye dissolving capacity of the liquid compositions of the invention as a function of the UFABLEND and butyl diglycol contents, respectively.

## Summary of the invention

**[0012]** In one aspect, the invention is directed to a liquid composition having synergistic dissolving effect, comprising

- a) at least one alkylene glycol ether of general formula  $(C_3-C_6\text{-alkyl})-(O-CH_2-CH_2)_n-OH$ , where the value of n is 1 to 5,
- b) at least one surfactant and
- c) water,

where the mass ratio of component a) to component b) ranges from 4:1 to 80:1.

**[0013]** In a further aspect the invention is directed to the use of the liquid composition according to the invention for cleaning various surfaces contaminated with dyestuff, heavy oil and/or bitumen.

## Detailed description of the invention

**[0014]** Component a) of the liquid composition of the invention is an alkylene glycol alkyl ether of unlimited water miscibility of general formula  $(C_3-C_6\text{-alkyl})-(O-CH_2-CH_2)_n-OH$ , where the value of n is 1 to 5, or a mixture thereof.

**[0015]** The  $C_3-C_6$ -alkyl group in the above formula is a linear or a branched saturated hydrocarbon group containing 3 to 6, preferably 4 or 5, most preferably 4 carbon atoms. The  $C_3-C_6$ -alkyl specifically includes propyl, isopropyl, n-butyl, sec-butyl, terc-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl groups, and the like. The hydrocarbon chain is preferably non-branched (normal). The alkylene glycol part of the above component a) can be mono-, di-, tri-, tetra- or pentaglycol. More particularly, examples like propyl glycol, propyl diglycol, propyl triglycol, butyl glycol, butyl diglycol, butyl triglycol, butyl tetraglycol, butyl pentaglycol, butyl hexaglycol, pentyl diglycol, hexyl glycol, hexyl diglycol, hexyl triglycol and so forth, can be mentioned.

**[0016]** The amount of component a) ranges from 40 to 80 % of the total mass of the composition.

**[0017]** Component b) of the composition of the invention can be anionic or non-ionic surfactant, or a mixture thereof. As surfactant, preferably Ufasan TEA (Brenntag Hungária Kereskedelmi Kft), 3EO (sodium lauryl ether sulfate, Biesterfeld Kft), Triton X100 (ICI Chemicals and Polymers Group), AOT (sodium salt of bis-(2-ethylhexyl) sulfosuccinate; Fluka), DAM (dialkyl ammonium-metasulfate; Stepan Company, Grenoble, France), Lutensol\*GD70 (BASF), UFABLEND (Unger Fabrikker A.S.), or the mixture of two or more of the above surfactants can be applied. Mixtures of Ufasan TEA and 3EO or Ufasan TEA and Triton X100 are the most preferred. The amount of component b) ranges from 1 to 10 % of the total mass of the composition.

**[0018]** The liquid compositions of the invention show synergistic dissolving capacity in the range of mass ratios of component a) to component b) between 4:1 and 80:1.

**[0019]** The liquid composition of the invention comprises water as component c) in an amount as required to 100%.

**[0020]** The liquid compositions of the invention may optionally comprise an alkali metal hydrogen carbonate such as sodium or potassium hydrogen carbonate or ammonium hydrogen carbonate as component d) in an amount up to 1.0 % of the total mass of the composition. Sodium hydrogen carbonate is preferred. After application of the liquid composition to the surface to be cleaned  $CO_2$  is liberated from component d) which promotes loosening of the pollutant layer.

**[0021]** The liquid compositions of the invention can be produced by mixing component a) alkylene glycol ether and component c) water; optionally adding component d) to the resulting alkylene glycol/water mixture during continuous, vigorous mixing, and homogenizing it; finally, adding component b) surfactant and mixing the system until complete dissolution is achieved. The so-obtained clear liquid has a pale yellow tone.

**[0022]** The alkylene glycol ethers used as component a) of the liquid compositions of the invention are known commercial compounds (produced by BASF for example), or can be produced by analogy with the known compounds, using methods known from the prior art.

**[0023]** The surfactants used as component b) of the liquid compositions of the invention are known commercial products as well. The alkali metal and ammonium hydrogen carbonates, used optionally as component d), are similarly known

compounds.

**[0024]** The liquid compositions of the invention are not fully homogeneous on a molecular level - although seem to be clear solutions -, but the systems contain nano-sized discontinuities the structure of which is not fully clarified up to date. Namely, the liquid compositions of the invention contain so-called clusters of the size of 10-12 nm, proven by us in dynamic light scattering experiments. While we do not wish to limit the present invention by theories, we suppose that the above cluster structure contributes to the synergistic effect and largely promotes loosening and dissolving of the dry dye coat layers, oily and tarry contaminations.

**[0025]** We have found that the liquid compositions (or complex mixtures) of the invention are well applicable to public buildings, street sculptures, privately owned objects (cars, doors and windows of buildings), transportation vehicles (bus, train, ship), infrastructure appliances of the transportation, that are coated with dye or oily contaminations.

**[0026]** According to this, in a further aspect the invention is directed to the use of the above liquid composition for cleaning surfaces contaminated with dyestuff, heavy oil and/or bitumen. The liquid composition of the invention is preferably used for cleaning graffiti dye contaminated surfaces. The surface to be cleaned can be smooth or porous, such as porous ceramic and/or plastered wall, or it can be granite, limestone, cast stone or concrete surface either.

**[0027]** Surprisingly, the combined dissolving effect of the components of the liquid composition of the invention - below demonstrated by examples - is synergistic, i.e., it is greater than the sum of the separate dissolving effects of the components. In addition to the above, the composition does not contain aromatic or aliphatic hydrocarbons thus, the environmental load effect thereof is minimal and after use it can be removed by washing with water or blowing with steam and can be collected. A further non-negligible advantage is that the concentration of the expensive surfactant component in the liquid composition of the invention is much smaller than in the known products used for similar purpose.

**[0028]** The following examples are provided so that the invention might be more fully understood. These examples are illustrative only and should not be construed as limiting the invention in any way.

## 1. Preparation example

**[0029]** Liquid compositions of the invention are prepared as shown below:

### Composition 1

| Component          | Amount (% by mass) |
|--------------------|--------------------|
| butyl diglycol     | 45.0               |
| UFABLEND           | 4.0                |
| NaHCO <sub>3</sub> | 0.5                |
| tap water          | 50.5               |

### Composition 2

| Component          | Amount (% by mass) |
|--------------------|--------------------|
| butyl diglycol     | 45.0               |
| UFABLEND           | 8.0                |
| NaHCO <sub>3</sub> | 0.5                |
| tap water          | 46.5               |

### Composition 3

| Component          | Amount (% by mass) |
|--------------------|--------------------|
| butyl diglycol     | 45.0               |
| Ufasan TEA         | 6.0                |
| NaHCO <sub>3</sub> | 1.0                |
| tap water          | 48.0               |

### Composition 4

| Component      | Amount (% by mass) |
|----------------|--------------------|
| butyl diglycol | 45.0               |
| Ufasan TEA     | 1.0                |
| 3EO            | 5.0                |

(continued)

**Composition 4**

| Component          | Amount (% by mass) |
|--------------------|--------------------|
| NaHCO <sub>3</sub> | 1.0                |
| tap water          | 48.0               |

**Composition 5**

| Component          | Amount (% by mass) |
|--------------------|--------------------|
| butyl diglycol     | 45.0               |
| Ufasan TEA         | 3.0                |
| Triton X100        | 3.0                |
| NaHCO <sub>3</sub> | 0.5                |
| tap water          | 48.5               |

**[0030]** We prepared the liquid compositions by mixing given amounts of butyl glycol and tap water; adding sodium hydrogen carbonate to the obtained butyl diglycol/water mixture while vigorous mixing, and homogenizing; finally, adding the given type and amount of surfactant, and mixing till it is completely dissolved as seen with the unaided eye. A clear liquid of pale yellow tone is obtained.

## 2. Determination of the dye dissolving effect of the compositions of the invention

**[0031]** We have evaluated the dissolving capacity of the liquid compositions on the surface of grains of a building material mix. We have prepared a coloured powder mix, designed to model the dye-sprayed plaster. A 0.1 % by mass solution of 30 g of acrylic dye in toluene was poured to 50 g of a powder mix (25 g Al<sub>2</sub>O<sub>3</sub> + 25 g SiO<sub>2</sub>) and left to stay for one hour while frequently stirring. The dense, coloured (red or blue, for example) suspension was filtered, washed with a few mL of toluene and dried at room temperature. After drying an appropriate coloured powder mix was obtained ready for quantitative characterization of the dissolving effect of the liquid compositions of the invention, as described below.

**[0032]** We have dissolved dyes from the acrylic dye contaminated mineral mixes using the liquid compositions of the invention and their components (alkylene glycol ethers and surfactants) alone as solvent under identical conditions. We added 10.0 mL each of the solvents to 0.5 g of solid in a glass sample holder with screwed cup and performed the solid-liquid extraction by shaking the suspension in a shaker for 30 minutes at a speed of 150 1/min. Next, the systems were left to settle for 1 day and then we measured the concentration of the dissolved dye in the extracts photometrically, against the pure solvents.

**[0033]** We determined the concentration of the dye in the individual samples ( $c_{\text{pract}}$ ) from the measured optical data with the help of calibration. Based on the composition we calculated the values of the additive concentration of dye ( $c_{\text{add}}$ ) using equation (1) below,

$$c_{\text{add}} = c_{\text{ag}}^{(m)} \cdot \Phi_{\text{ag}}^{(m)} + c_{\text{s}}^{(n)} \cdot \Phi_{\text{s}}^{(n)} + c_{\text{w}} \cdot \Phi_{\text{w}} \quad (1)$$

where

$C_{\text{ag}}^{(m)}$  is the concentration of dye extracted with alkylene glycol mixture of  $m$  components ( $m= 1,2,3,\dots$ ) and  $\Phi_{\text{ag}}^{(m)}$  is its volume fraction

$c_{\text{s}}^{(n)}$  is the concentration of dye extracted with surfactant mixture of  $n$  components ( $n= 1,2,3,\dots$ ) and  $\Phi_{\text{s}}^{(n)}$  is its volume fraction

$c_{\text{w}}$  is the concentration of dye extracted with tap water and  $\Phi_{\text{w}}$  is its volume fraction

**[0034]** The extraction experiments proved that - in case of the dyes examined by us - the dissolving capacity of the liquid compositions of the invention is higher than the sum of the separate dissolving capacities of the components (synergistic effect).

**[0035]** We represented the difference between the theoretical and the practical dissolving capacities by calculating and plotting the ratio  $(c_{\text{pract}} - c_{\text{add}})/c_{\text{add}}$ . The latter data show, how many times more dye is dissolved by the liquid

composition of the invention as compared to the theoretically expectable value (Figures 1 to 7).

**[0036]** In case of composition 1 as extraction liquid, for example, the calculation is:

The amount of butyl diglycol in composition 1 is 45.0 % by mass.

**[0037]** In case of additivity the dye concentration ( $c_{add}$ ) calculated using equation (1) is 29.5 mg/L.

**[0038]** The measured dye concentration ( $c_{pract}$ ) is 88.6 mg/L.

$$(c_{pract}-c_{add})/c_{add} = (88.6 - 29.5) / 29.5 = 2.002$$

so that composition 1 of the invention dissolved two times more dye than expected.

**[0039]** We determined also the dye dissolving capacity for compositions 2 to 5 of the invention according to the above. The results are summarized below.

| Sample        | $(c_{pract}-c_{add})/c_{add}$ |
|---------------|-------------------------------|
| Composition 1 | 2.002                         |
| Composition 2 | 2.196                         |
| Composition 3 | 2.411                         |
| Composition 4 | 2.038                         |
| Composition 5 | 2.271                         |

**[0040]** Compositions 1 to 5 had proven to be the most effective liquid compositions of the invention. Among them, the strongest synergistic effect has been found for composition 3, where the relative excess dissolving capacity ( $c_{pract}-c_{add}$ )/ $c_{add}$  was equal to 2.411. The relative excess dissolving capacity of compositions 1 to 5 of the invention and their synergistic effect is represented graphically in Figure 1.

**[0041]** Next, we examined how the change in the concentration of the individual components influences the dissolving capacity of the liquid compositions at constant values of the other parameters.

**[0042]** The surfactants applied to prepare the liquid compositions of the invention are: AOT, DAM, Lutensol\*GD70, UFABLEND.

**[0043]** The liquid compositions contained one, two or three of the above surfactants (surfactant mixtures) and the amount and ratio of them were varied as well within the separate series. The results are summarized shortly below.

**[0044]** If the liquid composition contains only AOT surfactant the synergistic effect is the strongest at lower (45 % by mass) butyl diglycol content. Synergistic effect is not observed in the presence of 80 or higher % by mass of butyl diglycol (Figure 2.a). The amount of the surfactant does not influence significantly the extent of the synergistic effect (Figure 2.b)

**[0045]** The situation is similar if another surfactant (DAM) is present besides AOT: stronger synergistic effect can be achieved with less (45 % by mass) butyl diglycol. Synergistic effect is not observed in the presence of more than 70 % by mass of butyl diglycol (Figures 3.a, 4.a, 5.a). The amount of DAM surfactant does not affect the dye dissolving capacity significantly at an AOT content of 1.5 % by mass. The strongest synergistic effect is obtained with 1.0 % by mass of DAM content at 0.5 % by mass of AOT concentration, and with 3.0 % by mass of DAM content at 1.0 % by mass of AOT concentration of (Figures 3.b, 4.b, 5.b).

**[0046]** Similarly, in the case of nonionic surfactant Lutensol\*GD70 the dye dissolving capacity of the liquid composition containing less (45 % by mass) butyl diglycol is strongest. Synergistic effect is not observed in the presence of more than 70 % by mass of butyl diglycol (Figure 6.a). Increase in the surfactant concentration slightly increases the synergistic effect (Figure 6.b).

**[0047]** In the presence of UFABLEND surfactant the increase in the surfactant concentration enhances the synergistic effect at 45 % by mass, and weakens at 60 % by mass of butyl diglycol (Figures 7.a-b).

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**[0048]**

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## Claims

1. A liquid composition having synergistic dissolving effect, comprising
  - a) at least one alkylene glycol ether of the general formula  $(C_3-C_6\text{-alkyl})-(O-CH_2-CH_2)_n-OH$ , where the value of n is 1 to 5,
  - b) at least one surfactant and
  - c) water,
 where the mass ratio of component a) to component b) ranges from 4:1 to 80:1.
2. The liquid composition of claim 1 wherein the amount of component a) ranges from 40 to 80 % by mass and the amount of component b) ranges from 1 to 10 % by mass of the total composition.
3. The liquid composition of claims 1 or 2, comprising alkali metal or ammonium hydrogen carbonate as further component d).
4. The liquid composition of claim 3 wherein the amount of component d) ranges from 0.5 to 1.0 % by mass of the total composition.
5. The liquid composition of claims 3 or 4 comprising sodium hydrogen carbonate as alkali metal hydrogen carbonate.
6. The liquid composition of any one of claims 1 to 5 comprising anionic and/or non-ionic surfactant as surfactant.
7. The liquid composition of claim 6 wherein the surfactant is Ufasan TEA, 3EO, Triton X100, AOT, DAM, Lutensol\*GD70, UFABLEND, or a mixture of two or more of the above surfactants.
8. The liquid composition of any one of claims 1 to 7, comprising butyl glycol, butyl diglycol, butyl pentaglycol, propyl glycol, propyl diglycol, propyl triglycol or the mixture thereof as component a).
9. The liquid composition of any one of claims 1 to 8, comprising 45.0 % by mass of butyl diglycol, 6 % by mass of surfactant, 0.5 - 1.0 % by mass of sodium hydrogen carbonate and 48.0 - 48.5 % by mass of water.
10. The liquid composition of claim 9 comprising Ufasan TEA, a mixture of Ufasan TEA and Triton X100 or a mixture of Ufasan TEA and 3EO as surfactant.

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11. The liquid composition of any one of claims 1 to 8 comprising 45.0 % by mass of butyl diglycol, 4-8 % by mass of surfactant, 0.5 % by mass of sodium hydrogen carbonate and 46.5 - 50.5 % by mass of water.
12. The liquid composition of claim 11 comprising UFABLEND as surfactant.
13. The use of the liquid composition of any one of claims 1 to 12 for cleaning surfaces contaminated with dyestuff, heavy oil and/or bitumen.
14. The use of claim 13 wherein the surface is contaminated with graffiti dyes.
15. The use of claims 13 or 14 wherein the surface is at least one selected from the group consisting of porous ceramic, plastered wall, granite, lime stone, cast stone and concrete surfaces.



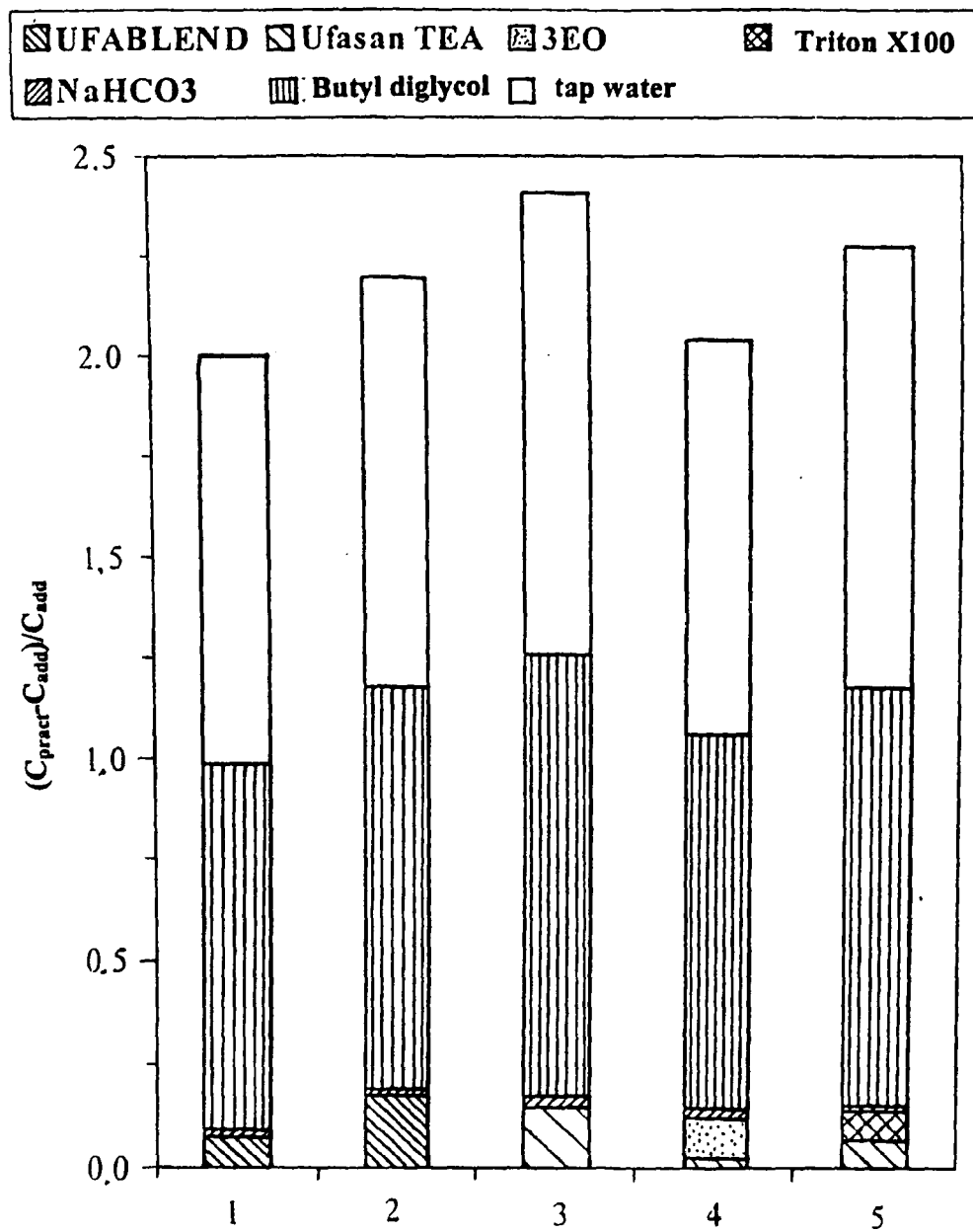
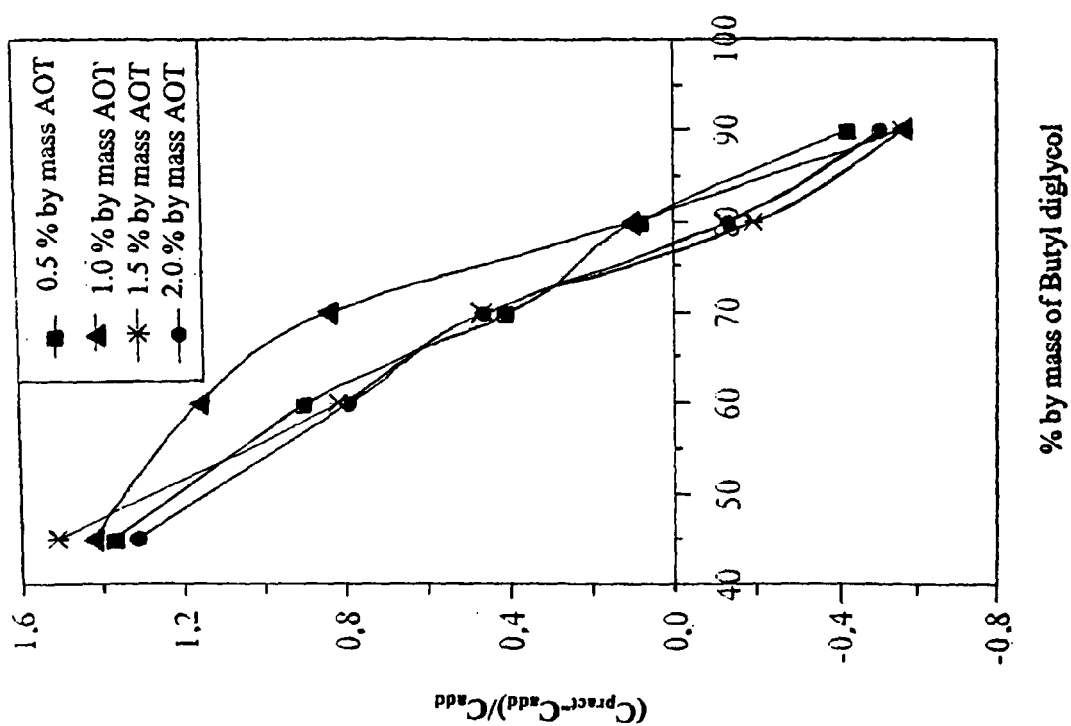
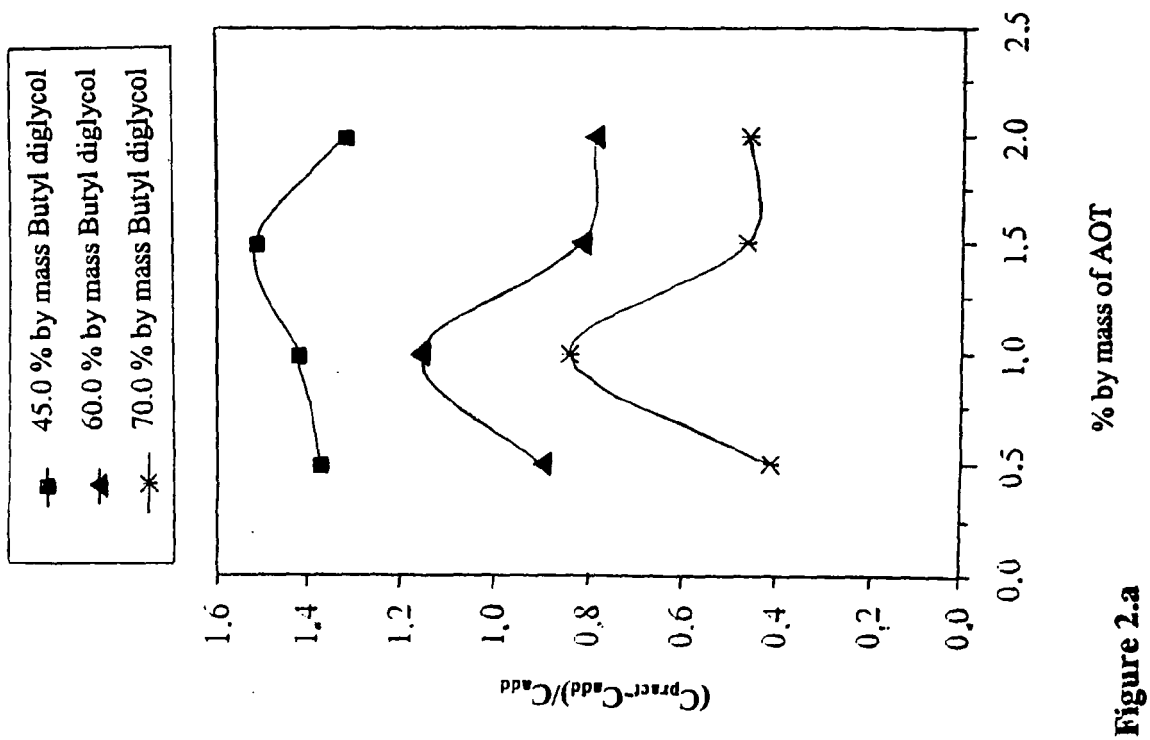


Figure 1



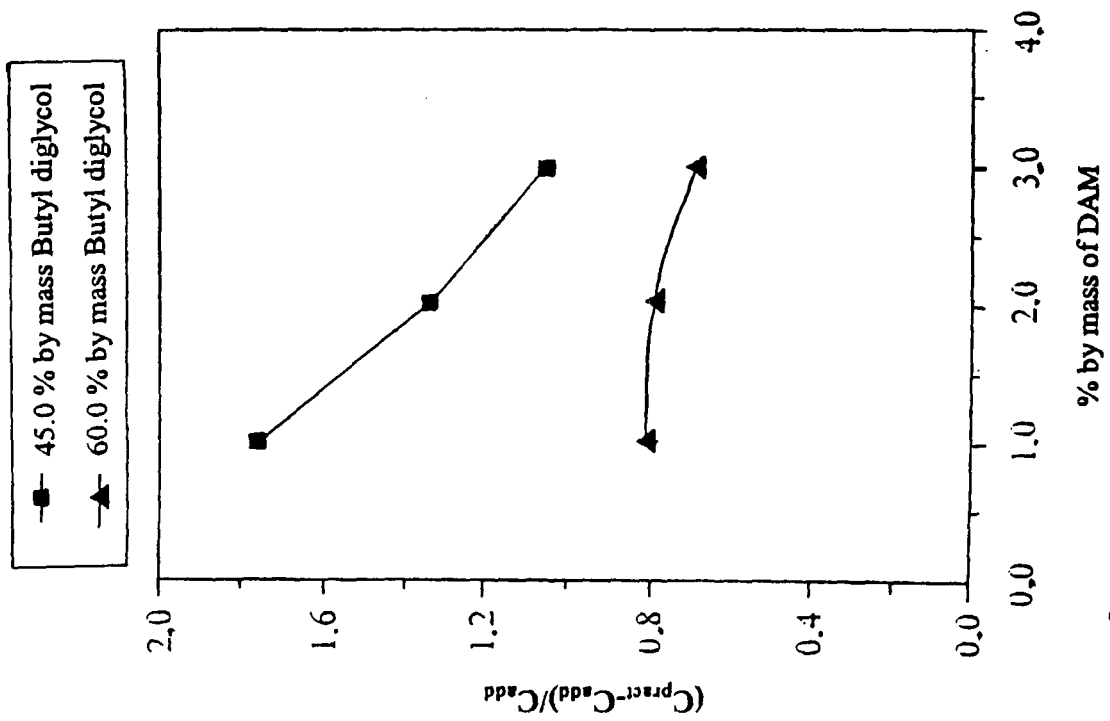


Figure 3.a

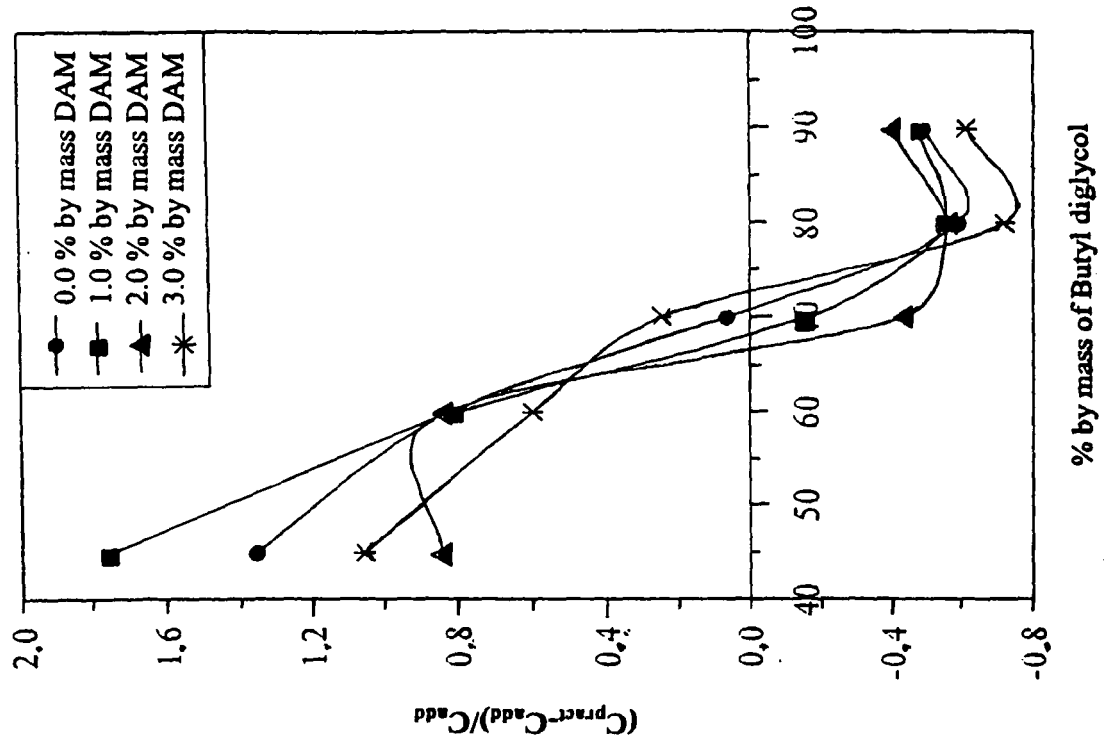
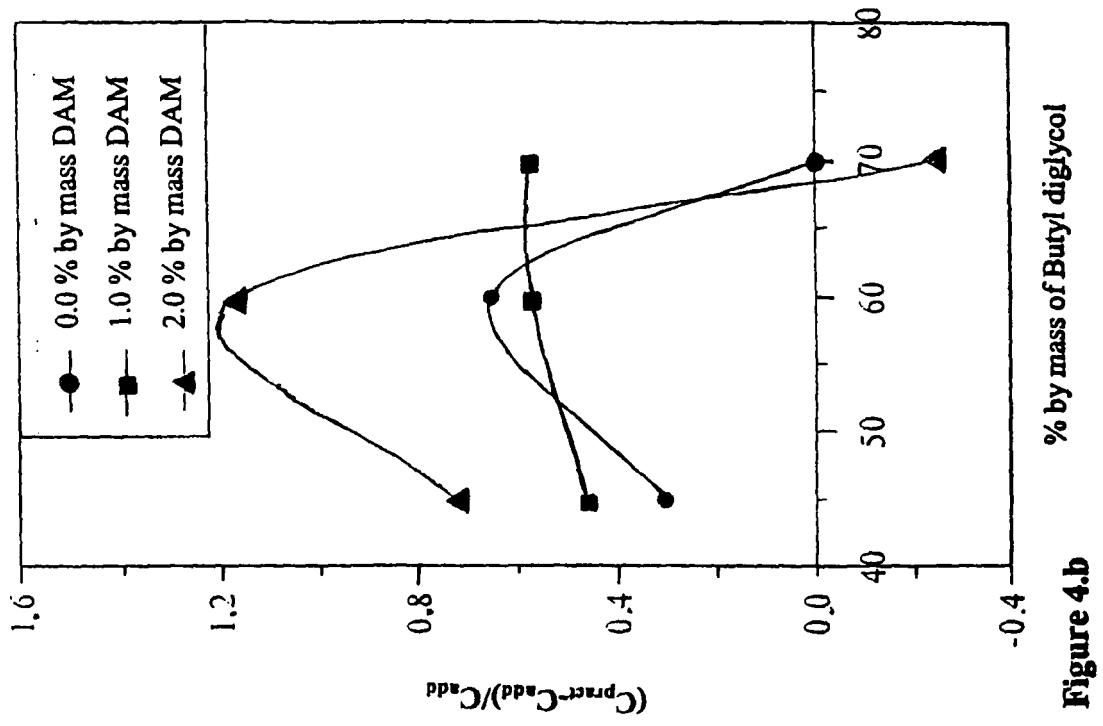
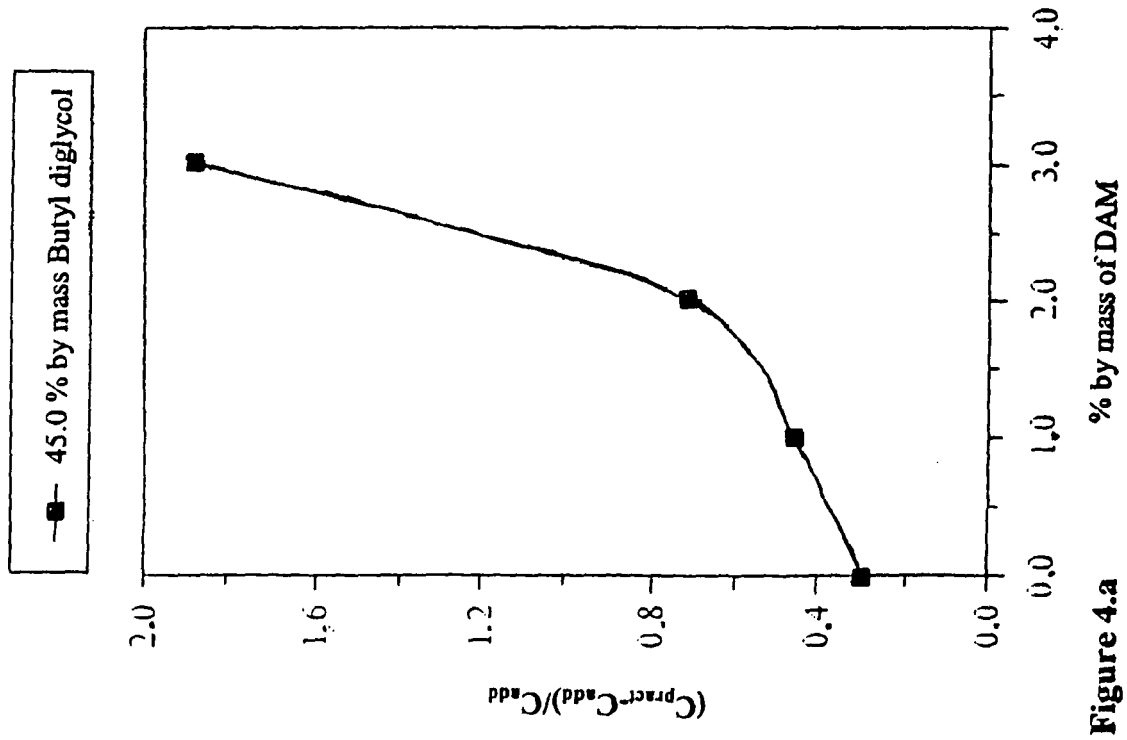


Figure 3.b



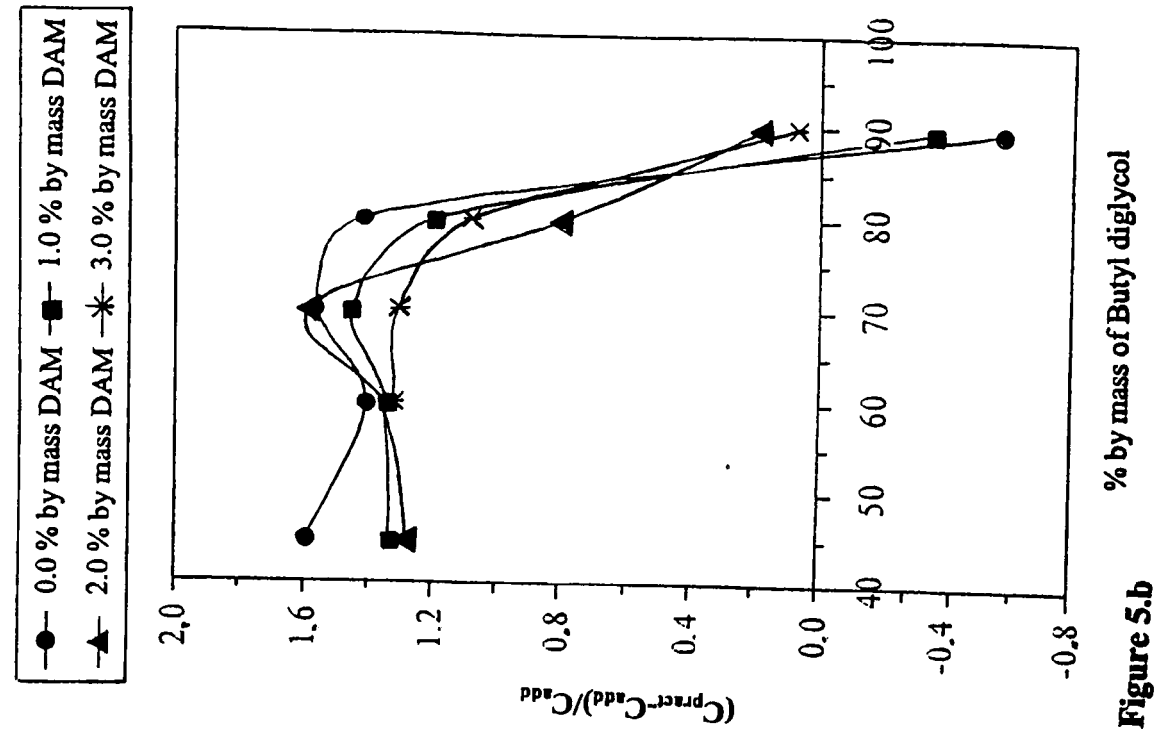
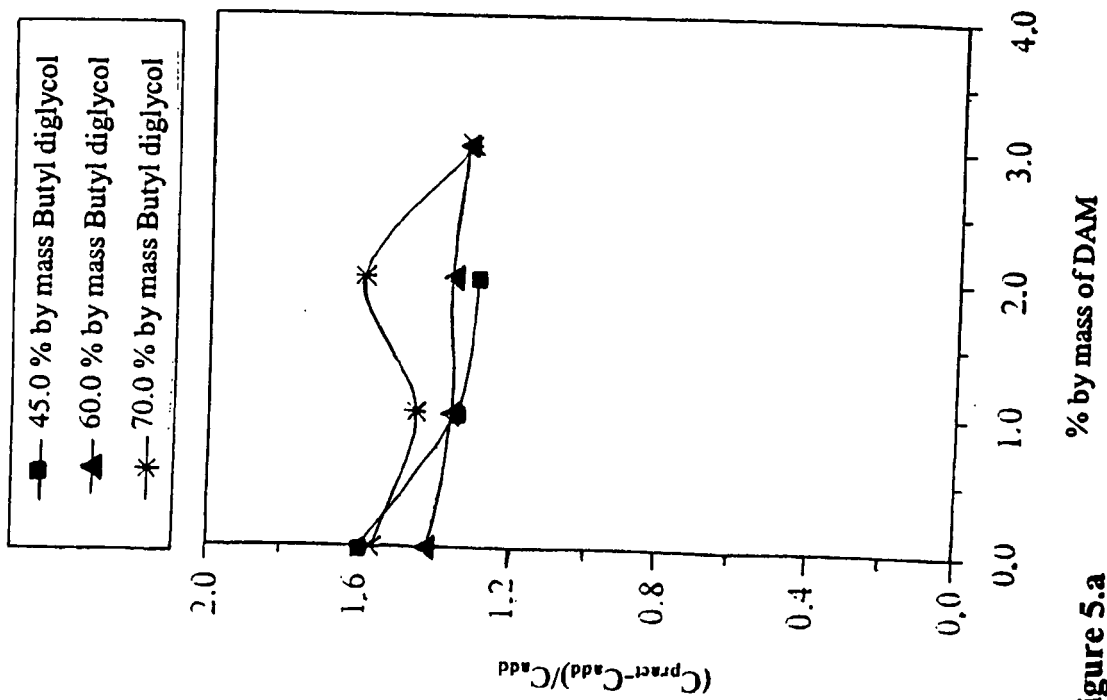


Figure 5.a



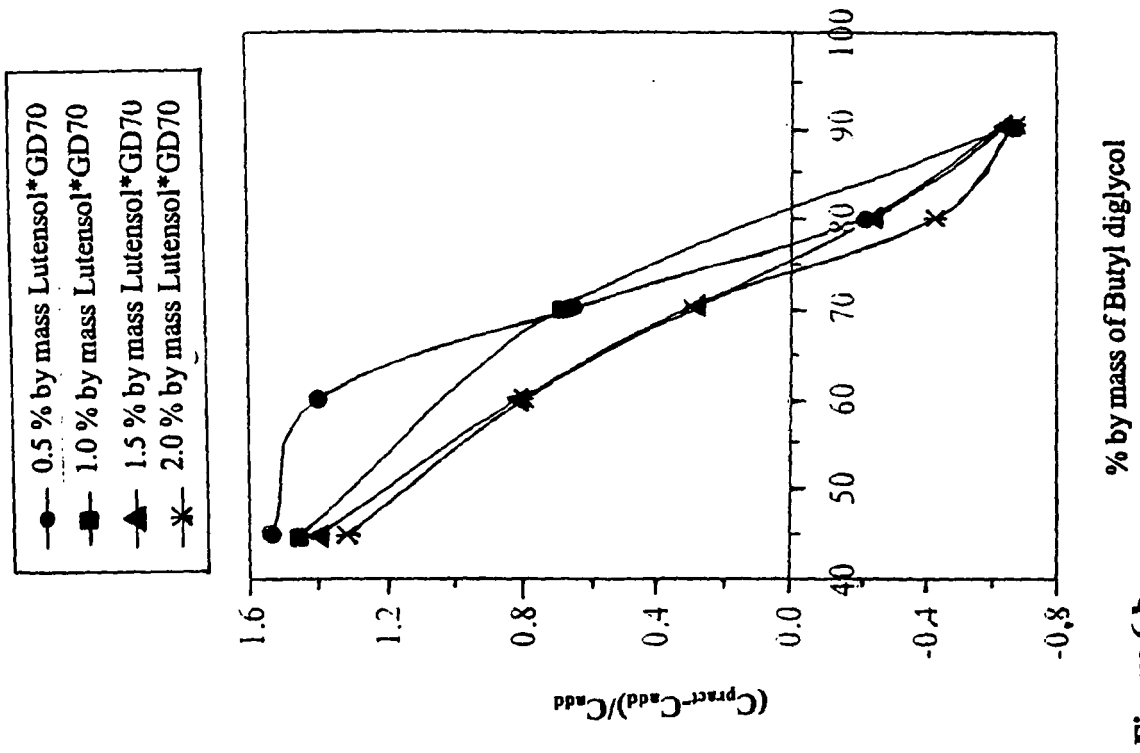


Figure 6.b

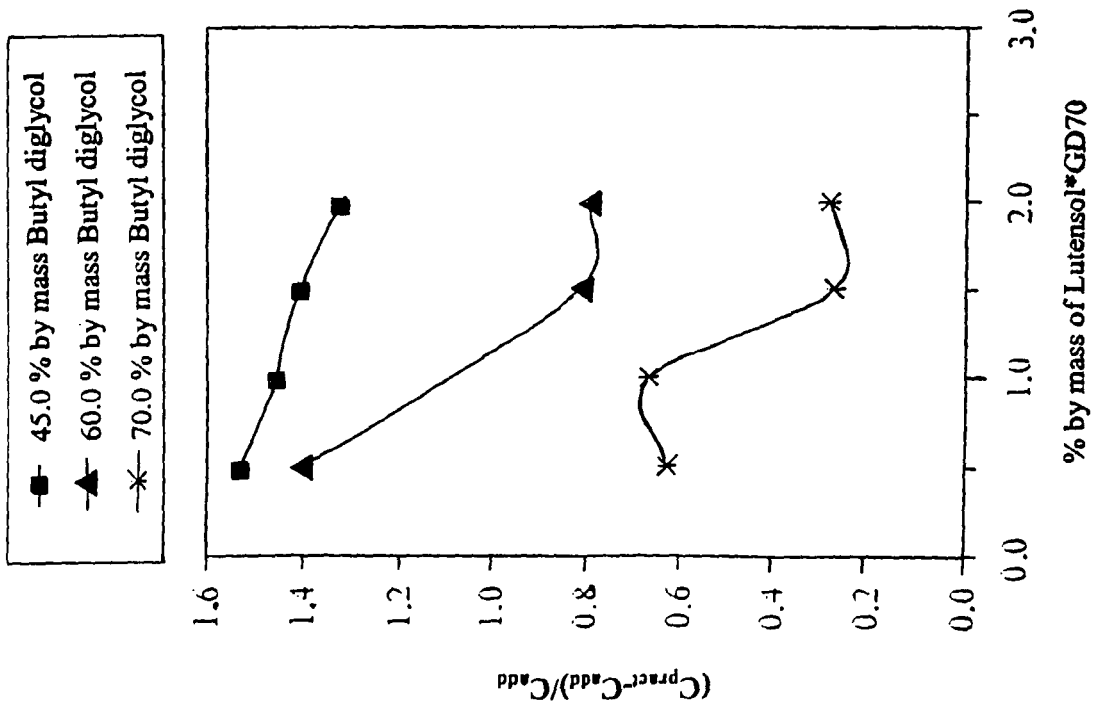


Figure 6.a

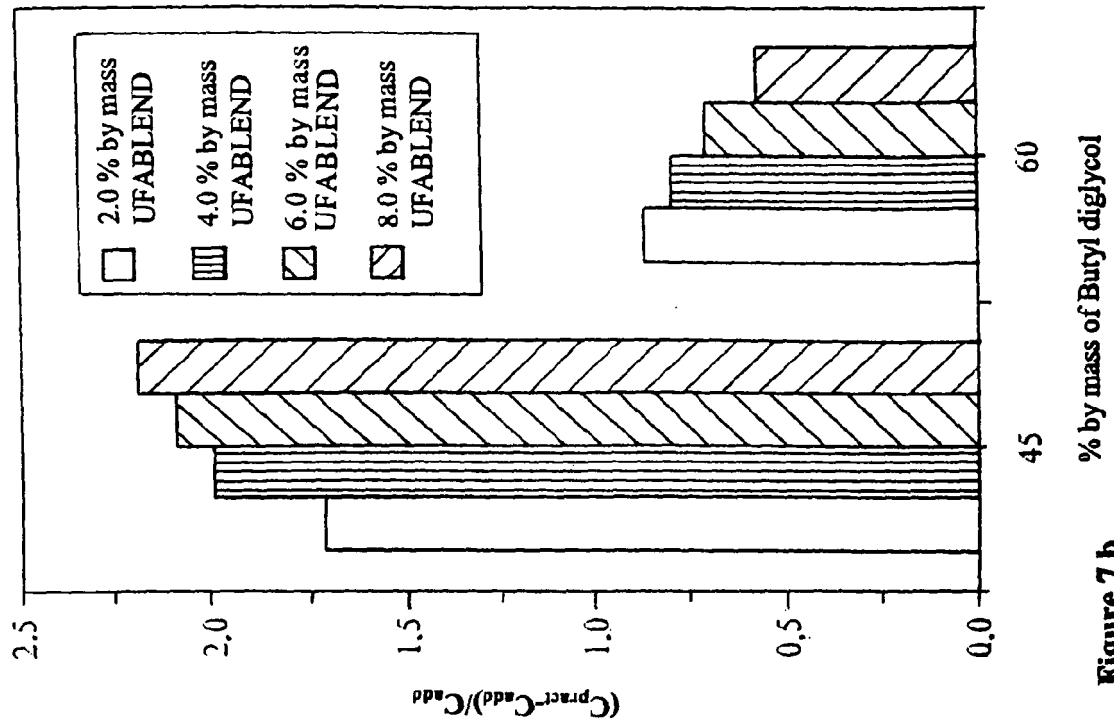


Figure 7.b

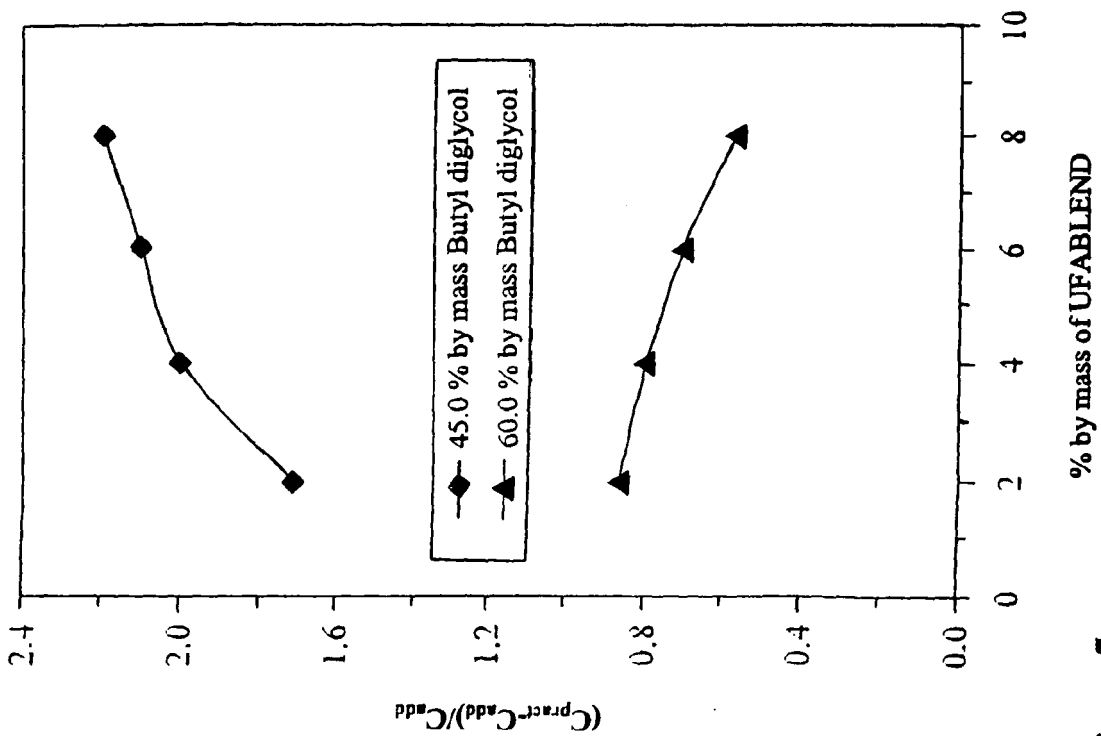


Figure 7.a



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| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                       |                                                                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Category                                                                                                                                                                                                                                               | Citation of document with indication, where appropriate, of relevant passages                                                                                                                                                                                                 | Relevant to claim                                                                                                                                                                                                                                                                     | CLASSIFICATION OF THE APPLICATION (IPC)                                       |
| X                                                                                                                                                                                                                                                      | WO 00/40680 A2 (UNION CARBIDE CHEM PLASTIC [US]) 13 July 2000 (2000-07-13)<br>* claims *<br>* examples 4-6,8-11 *<br>* Control example *<br>* page 2, last paragraph - page 5, paragraph 3 *<br>* page 1, paragraph 1 *<br>-----                                              | 1,6-7,<br>13,15                                                                                                                                                                                                                                                                       | INV.<br>C11D3/20<br>C11D11/00<br>C11D1/83<br>C11D1/02<br>C11D1/66<br>C11D3/10 |
| X                                                                                                                                                                                                                                                      | EP 0 506 087 A2 (UNION CARBIDE CHEM PLASTIC [US])<br>30 September 1992 (1992-09-30)<br>* Control ex. II: ; page 6 *<br>* page 6, line 26 - page 7, line 38 *<br>* page 8: Control Ex. V and VI *<br>* page 10: Control Ex. IX and X *<br>-----                                | 1,6-8,13                                                                                                                                                                                                                                                                              | ADD.<br>C11D1/29<br>C11D1/12<br>C11D1/22<br>C11D1/72                          |
| X                                                                                                                                                                                                                                                      | US 4 808 235 A (WOODSON JEFFREY B [US] ET AL) 28 February 1989 (1989-02-28)<br>* claims *<br>* example 1 *<br>* column 2, line 65 - column 3, line 44 *<br>* column 3, line 65 - column 4, line 37 *<br>* column 5, line 1 - line 21 *<br>* Formulations 1, 2, 4-6 *<br>----- | 1-2,6-8,<br>13                                                                                                                                                                                                                                                                        | TECHNICAL FIELDS<br>SEARCHED (IPC)<br><br>C11D                                |
| X                                                                                                                                                                                                                                                      | US 6 432 899 B1 (SJOSTROM TERRY D [US])<br>13 August 2002 (2002-08-13)<br>* examples; tables 1,3 *<br>* column 1, line 7 - line 24 *<br>-----                                                                                                                                 | 1,6-8                                                                                                                                                                                                                                                                                 |                                                                               |
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| The present search report has been drawn up for all claims                                                                                                                                                                                             |                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                       |                                                                               |
| Place of search<br>The Hague                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                               | Date of completion of the search<br>17 February 2010                                                                                                                                                                                                                                  | Examiner<br>Neys, Patricia                                                    |
| CATEGORY OF CITED DOCUMENTS<br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |                                                                                                                                                                                                                                                                               | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>.....<br>& : member of the same patent family, corresponding document |                                                                               |

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| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                       |                                                      |                                         |
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| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | WO 99/25798 A1 (HENKEL CORP [US]; SJOSTROM TERRY D [US]) 27 May 1999 (1999-05-27)<br>* tables 1,3 *<br>* page 9, line 17 - line 22 *                                                                                                  | 1,6-8                                                |                                         |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | US 2006/063689 A1 (NETHERTON JASON J [US]) 23 March 2006 (2006-03-23)<br>* claims 1,2,6,10,12, *<br>* examples 1-4 *<br>* page 1, paragraph 3 *<br>* page 2, paragraph 19 - paragraph 20 *<br>* page 3, paragraph 44 - paragraph 47 * | 1,6-8, 13-15                                         |                                         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | US 6 617 298 B1 (MORROW DENNIS S [US] ET AL) 9 September 2003 (2003-09-09)<br>* claims *<br>* examples *<br>* column 1, line 6 - line 8 *                                                                                             | 1-15                                                 |                                         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | WO 01/21719 A1 (COGNIS CORP [US]) 29 March 2001 (2001-03-29)<br>* the whole document *                                                                                                                                                | 1-15                                                 |                                         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | WO 2007/076337 A2 (NOVOZYMES BIOLOG INC [US]) 5 July 2007 (2007-07-05)<br>* example 3 *                                                                                                                                               | 1-15                                                 |                                         |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                       |                                                      | TECHNICAL FIELDS SEARCHED (IPC)         |
| Place of search<br>The Hague                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                       | Date of completion of the search<br>17 February 2010 | Examiner<br>Neys, Patricia              |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>&amp; : member of the same patent family, corresponding document</p> |                                                                                                                                                                                                                                       |                                                      |                                         |

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