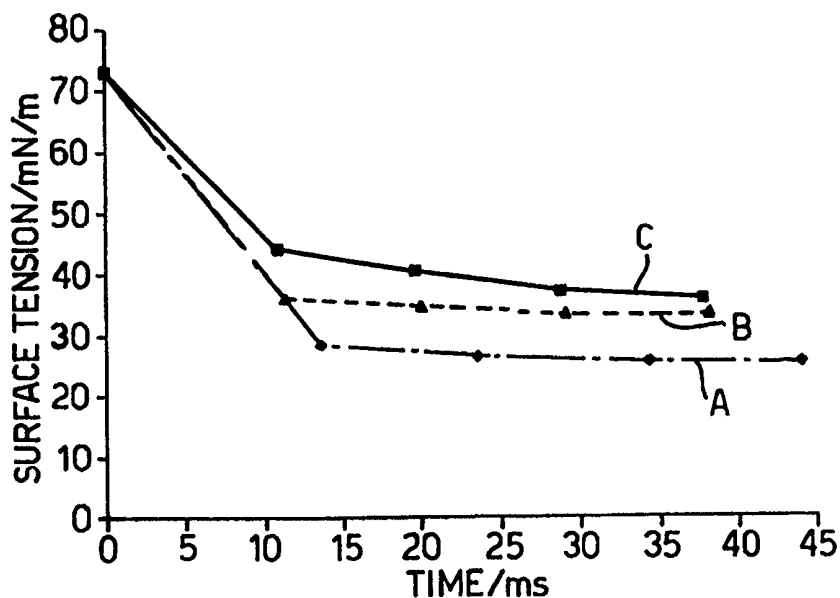




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<p>(21) International Application Number: PCT/GB98/03360 (22) International Filing Date: 10 November 1998 (10.11.98) (30) Priority Data: 9723916.4 12 November 1997 (12.11.97) GB (71) Applicant (for all designated States except US): KIDDE-GRAVINER LIMITED [GB/GB]; Pentagon House, Sir Frank Whittle Road, Derby (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CHATTAWAY, Adam [GB/GB]; 13 Lark Avenue, Moormede, Staines, Middlesex TW18 4RX (GB). PREECE, Stephen, Richard [GB/GB]; White Cottage, Roundbush, Aldenham, Watford, Hertfordshire WD2 8BH (GB). (74) Agent: MATHISEN, MACARA & CO.; The Coach House, 6-8 Swakeleys Road, Ickenham, Uxbridge, Middlesex UB10 8BZ (GB).</p>	<p>(81) Designated States: US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>	

(54) Title: FIRE OR EXPLOSION SUPPRESSANTS AND METHODS



(57) Abstract

A fire or explosion suppressant is described comprising water or an aqueous alkali metal salt solution together with a surfactant. The surfactant is selected so as to be fast-acting – that is, so that upon dispersion of the water or water-based solution towards the fire or explosion (e.g. in a jet or under atomisation), the surfactant acts to produce a surface tension value which becomes low (preferably at least as low as about 25 mN/m) within the time taken for the dispersed water to reach the fire or explosion (less than 50 ms and preferably less than 20 ms). Examples of suitable surfactants are disclosed.

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FIRE OR EXPLOSION SUPPRESSANTS AND METHODS

The invention relates to fire or explosion suppressants or methods. More particularly, the invention relates to such suppressants and methods comprising or using water. Fire or explosion suppressants according to the invention, and to be described in more detail below by way of example only, comprise water with an additive comprising a surfactant.

According to the invention, there is provided a fire or explosion suppressant, comprising a water-based solution containing a surfactant characterised in that the surfactant is capable upon dispersion of the solution of producing a predetermined value for the surface tension which becomes at least as low as about 25 mN/m in less than 50 milliseconds.

According to the invention, there is provided a method of suppressing a fire or explosion, comprising the steps of adding to a water-based solution a surfactant and dispersing the solution to the fire or explosion, characterised in that the surfactant is capable upon dispersion of the solution of producing a predetermined value for the surface tension which becomes at least as low as about 25 mN/m in less than 50

milliseconds.

Fire or explosion suppressants embodying the invention, and methods of suppressing fires or explosions according to the invention, will now be described, by way of example only, with reference to the accompanying diagrammatic drawings in which:

Figure 1 shows a volume of water-based suppressant for explaining the operation of suppressants according to the invention;

Figure 2 is an enlarged view of part of Figure 1;

Figure 3 shows an oscillating jet arrangement for testing the effectiveness of various surfactants;

Figure 4 is a section on the line IV-IV of Figure 3; and

Figure 5 is a graph for comparing the effectiveness of various surfactants.

The fire or explosion suppressants to be described in more detail use water. Water is of course a well-known fire or explosion suppressant. It acts only as a physically-acting agent,

producing a heat absorption or extraction effect without any chemical suppression mechanism. However, it has a high surface tension and high interfacial tensions on most materials and is therefore a poor wetting agent. On most solid surfaces, water remains as discrete droplets (with a contact angle greater than 90°) and therefore does not effectively wet the surface. Therefore, heat transfer from the burning substance to the water would be impeded - because this depends on the surface area of contact - and thus the suppressant action would be poor.

It is advantageous to apply water as a suppressant in the form of very small water droplets (having a diameter of less than 100 and preferably less than 50 micrometres for example), because such droplets have a high specific surface area. However, because of its high surface tension it is quite difficult to atomise water to produce droplets of this size. If the droplets are to be produced by atomising water using pneumatic dispersion through a nozzle, it may be necessary to use very high pressures (greater than 50 bar) or low flow rates, both of which raise difficulties in practice.

It is therefore known to add surfactants to water in order to reduce its surface tension with a view to overcoming the above

disadvantages. By reducing surface tension, surfactants improve the wetting action of water. More specifically, reduction of surface tension can have a beneficial effect on median droplet size. Thus, it has been empirically shown that

$$\frac{D_{vm,solution}}{D_{vm,water}} = \left(\frac{\gamma_{solution}}{73}\right)^{0.5} \left(\frac{\mu_L}{1.0}\right)^{0.2} \left(\frac{1.0}{\rho_L}\right)^{0.3} \quad [1]$$

[see Perry, R.H. and Green, D.W., Eds. *Perry's Chemical Engineer's Handbook*. Fifth ed. 1984, McGraw-Hill: New York]

where

D_{vm}	=	volume median droplet diameter
γ	=	surface tension, mN/m
μ_L	=	solution liquid viscosity, cP
ρ_L	=	solution liquid density, g/cm ³

Equation 1 shows that the parameter with the greatest effect on droplet size is surface tension (γ).

Figure 1 shows a volume of water 5 with the water/air interface being shown as 6. Surfactant molecules are shown (purely diagrammatically, of course) as 8. Each surfactant molecule

comprises a hydrophilic "head" 8A and a hydrophobic "tail" 8B. The surfactant molecules 8 thus congregate along the interface or surface 6 with their "tails" 8B extending through the surface of the water, and thus reducing the surface tension forces acting there. In addition, however, assuming a sufficient concentration of the surfactant material, other surfactant molecules will form micelles indicated diagrammatically in Figure 1 at 10. Figure 2 shows one of the micelles 10 in enlarged (and, again, purely diagrammatic) form. Because of the hydrophilic "heads" 8A and hydrophobic "tails" 8B, the surfactant molecules congregate in groups or micelles 10 which are typically spheroidal in shape, with their "tails" 8B extending towards each other and to the centre of the micelles forming central areas in each micelle from where the water is repelled by the hydrophobic action of the "tails" of the surfactant molecules. In the general case, there are many micelles in a volume of water.

Because the surfactant molecules in the micelles 10 are not effective at the surface 6 of the water, they are not acting to reduce the surface tension of the water. The surface tension-reducing action is only performed by the surfactant molecules at the surface as shown in Figure 1. In Figure 1, it is assumed that the surface 6 of the water is substantially fully occupied

by the surfactant molecules. However, when the water is dispersed (for example, directed as a jet towards a fire) and, in particular, when it is atomised into droplets, new water/air interfaces are created. In order that the surfactant molecules can be effective in such changed circumstances for reducing the surface tension of the water, the molecules have to diffuse to the new interfaces - in particular, they have to diffuse to the interfaces from the micelles. In order for the surfactants to be effective in reducing the surface tension of the water in conditions of fire or explosion - in other words, in order for the surfactant molecules to be in position to reduce the surface tension of the water when it is applied to the fire or explosion - the time taken for the surfactant molecules to diffuse from the micelles to the new surfaces must be shorter than the time taken for the water to travel from the point of discharge (e.g. the atomising nozzle) to the fire. In many practical applications, this time period is less than 50ms. Therefore, in accordance with the invention, surfactants capable of lowering the surface tension of the water within the same order of time scale are added to water-based fire or explosion suppressant solutions. By "fast-acting" is meant surfactants which act within a time period of less than 50ms and preferably of the order of 10 to 20ms, and which reduce the surface tension at least to the order

of 30mN/m and preferably 25mN/m.

The water may be pure water or it may be water containing an alkali metal salt such as potassium bicarbonate, potassium lactate, potassium acetate or potassium citrate.

Specific examples of suitable surfactants will be discussed below. Generally, though, the surfactant has the structural formula RXM.

Within this structural formula, M is a cation of an alkali metal (lithium, sodium, potassium, rubidium, caesium) or of a protonated amine.

X in the structural formula RXM is an anionic group. Suitable groups are a sulphate ($-\text{OSO}_3$), a sulphonate ($-\text{SO}_3$) or a carboxylate ($-\text{CO}_2$); the sulphate is preferred.

R in the formula RXM is an alkyl (preferably, a branched chain alkyl group) or is an alkylaryl group, in each case containing four to twenty carbon atoms and preferably at least one atom of silicon. A preferred example for R contains the trimethylsilyl group ($(\text{CH}_3)_3\text{Si}-$).

The molecular weight of the RX fragment should be below 400 Daltons and preferably below 300 Daltons.

A preferred example of a suitable surfactant is a trimethylsilylbutane sulphate salt of the form $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-OSO}_3^-\text{M}^+$, where M is an alkali metal cation of sodium or potassium or of a protonated amine.

The water-based solution may be pure water or water containing an alkali metal salt such as potassium bicarbonate, potassium lactate, potassium acetate or potassium citrate. More specific examples are:-

(a) water containing potassium bicarbonate in the concentration range 1 - 24 weight %, preferably 15 - 24 weight %;

(b) water containing potassium acetate in the concentration range 5 - 60 weight %, preferably 40 - 60 weight %;

(c) water containing potassium lactate in the concentration range 5 - 60 weight %, preferably 40 - 60

weight %;

(d) water containing potassium citrate, in the concentration range 5 - 60 weight %, preferably 40 - 60 weight %.

Because the surfactants operate to reduce the surface tension within such a short time scale, the droplet sizes of the water are much smaller, producing better heat transfer from the fire or explosion and thus a better suppressant effect. The rapid reduction in the surface tension facilitates further atomisation of the droplets as they move through the air from the discharging nozzle to the fire or explosion (enhanced droplet stripping). The droplets have improved wetting ability for hot surfaces (e.g. the hot surfaces of clutter within a room or container such as an engine compartment of a vehicle or a crew compartment of a military vehicle), thus producing enhanced heat transfer.

The rapid reduction of surface tension also is particularly advantageous for explosion suppression applications.

Tests have been carried out to examine the effectiveness of various surfactants and their ability to reduce the surface

tension in the short timescales required. Because of these short timescales, measurement of equilibrium surface tension values may not be of significance, because for some surfactants the equilibrium surface tension value may not be reached until a relatively long time has elapsed - possibly tens of seconds. What is important in the present instance is the surface tension value which is reached after time periods of the order of 10 to 25ms; it is therefore necessary to measure the surface tension dynamically. A suitable method is to use an oscillating jet as shown in Figures 3 and 4. Here, the liquid under test (that is, the water-based solution containing a particular surfactant) is discharged through a nozzle 12 having a non-circular orifice 14, which is elliptical in cross-section in this example. The resultant jet 16 will be mechanically unstable: its initial cross-section will be non-circular (corresponding with the shape of the orifice) and will collapse to a circular cross-section which has the lower surface energy. However, the momentum of the jet will carry the cross-section beyond the desired circular one to a non-circular form. This process continues, producing oscillations in the jet which continue until insufficient momentum remains to maintain a coherent jet, when collapse into droplets occur. Figure 3 shows the form of jet produced when the orifice is elliptical.

In the oscillating jet, λ is taken as the distance between two successive maxima (or minima) in the jet. The surface tension γ relative to water at a particular value for γ is found from the relationship:-

$$\gamma_s = \gamma_w [\lambda_w / \lambda_s]^2 \quad [2]$$

where λ = wavelength (distance between successive nodes)

γ is surface tension (mN/m)

and the subscript S denotes surfactant solution and the subscript W denotes pure water.

The time taken to reach a particular surface tension value may be calculated by measuring the flow rate at the nozzle 12 and the distance of a node from the nozzle.

Figure 5 shows a graph illustrating the results produced when testing three different solutions - that is, solutions which contain respectively different surfactants in water, all at 0.5% by volume.

The surfactant which produces curve A causes the solution to reach a low value of surface tension very quickly - a value of

about 26.5mN/m after 20ms and slightly less after 40ms.

The surfactant which produces curve B also reduces surface tension quickly but the value of the surface tension reached after about 20ms is higher, at 35.0mN/m and about 32.6mN/m after 40ms.

Finally, the surfactant which produces curve C does not reduce the surface tension very quickly and the value of the surface tension reached after about 20ms is higher still at about 40mN/m and about 36.2mN/m after 40ms, although in this particular case the equilibrium surface tension reached after a very much longer period of time is 22.6mN/m.

In these tests, therefore, it is the surfactant which produces curve A which is suitable for reducing the surface tension sufficiently quickly and to a sufficiently low value. The surfactants producing curves B and C are not satisfactory because the value of surface tension is too high (curve B) or the reduction in surface tension is too slow (curve C). In Figure 5, the surfactant producing curve A is a trialkylammonium salt of trimethylsilylbutane sulphate (referred to below as SURFACTANT A), the surfactant producing curve B the sodium salt of is

dodecylbenzenesulphonic acid (referred to below as SURFACTANT B), and the surfactant producing curve C is a cationic fluorine-containing surfactant ($C_6F_{13}CH_2CH_2SCH_2CH_2CH(OH)CH_2N^+(CH_3)_3Cl^-$ (referred to below as SURFACTANT C)).

In a further set of tests, various extinguishants have been tested for extinguishing fires in obstructed or cluttered spaces such as military vehicle crew compartments. These tests were carried out on water-based extinguishant solutions intended to replace Halon. The Table below shows tests carried out on a number of different extinguishant solutions. The tests were carried out under standard conditions (standard volumes containing standard fires) representing the characteristics of and in crew compartments. In some cases, clutter was present in the volumes and in others there was no such clutter. In each case, the minimum quantity of the suppressant (in kg/m^3) to achieve suppression was measured.

TABLE ONE

Clutter Present?	Suppressant	Minimum Suppressant Quantity (kg/m^3)
No	Halon 1301	0.45
Yes	Halon 1301	0.45

Clutter Present?	Suppressant	Minimum Suppressant Quantity (kg/m ³)
No	Water + potassium lactate	0.45
Yes	Water + potassium lactate	0.8
Yes	Water + potassium lactate + SURFACTANT A	0.45

The tests show that the addition of SURFACTANT A (a trialkylammonium salt of trimethylsilylbutane sulphate) improves the operation of the extinguishant solution (in particular, its atomisation) to the extent where its fire suppression performance is equal to that of Halon 1301.

Tests have also shown that fast-acting surfactants as defined herein, such as SURFACTANT A mentioned above, are effective in significantly improving the effectiveness of water and water-based extinguishants in suppressing Class A fires (cellulose-type material such as wood and paper). Without the addition of such surfactants the ability of such extinguishants to suppress such fires is hampered by their high surface tension and thus their inability to wet the surfaces of the burning material properly. The addition of the fast-acting surfactant ensures that this problem is overcome by lowering the surface tension sufficiently and within the timescale of the suppression process. In a particular series of tests a standardised hydrocarbon fire was

established in a wooden "crib" in a test chamber. Tests were carried out using a succession of extinguishants under standardised conditions to check whether actual cooling of the crib was achieved by the extinguishant. The extinguishants were sprayed from a predetermined distance to the crib, the time of travel from the nozzle to the crib being about 19ms. In each case, the extinguishant was pure water but with the addition of 0.5% of a particular surfactant. The following results were achieved:

Added surfactant	Cooling of crib?
SURFACTANT C	No
SURFACTANT B	No
SURFACTANT A	Yes

CLAIMS

1. A fire or explosion suppressant, comprising a water-based solution containing a surfactant characterised in that the surfactant is capable upon dispersion of the solution of producing a predetermined value for the surface tension which becomes at least as low as about 25 mN/m in less than 50 milliseconds.

2. A method of suppressing a fire or explosion, comprising the steps of adding to a water-based solution a surfactant and dispersing the solution to the fire or explosion, characterised in that the surfactant is capable upon dispersion of the solution of producing a predetermined value for the surface tension which becomes at least as low as about 25 mN/m in less than 50 milliseconds.

3. A suppressant or method according to claim 1 or 2, in which the predetermined surface tension value is reached within less than 20 milliseconds.

4. A suppressant or method according to any preceding claim, in which the water-based solution is pure water.

5. A suppressant or method according to any one of claims 1 to 4, in which the water contains an alkali metal salt.
6. A suppressant or method according to any preceding claim, in which the alkali metal salt is present in a concentration greater than 5 weight %.
7. A suppressant or method according to any preceding claim, in which the alkali metal salt is a potassium salt.
8. A suppressant or method according to claim 5, in which the alkali metal salt is potassium bicarbonate.
9. A suppressant or method according to claim 8, in which the potassium bicarbonate is present in the concentration range 1 - 24 weight %.
10. A suppressant or method according to claim 8, in which the potassium bicarbonate is present in the concentration range 15 - 24 weight %.
11. A suppressant or method according to claim 5, in which the alkali metal salt is potassium acetate.

12. A suppressant or method according to claim 11, in which the potassium acetate is present in the concentration range 5 - 60 weight %.

13. A suppressant or method according to claim 8, in which the potassium acetate is present in the concentration range 40 - 60 weight %.

14. A suppressant or method according to claim 5, in which the alkali metal salt is potassium lactate.

15. A suppressant or method according to claim 14, in which the potassium lactate is present in the concentration range 5 - 60 weight %.

16. A suppressant or method according to claim 15, in which the potassium lactate is present in the concentration range 40 - 60 weight %.

17. A suppressant or method according to claim 5, in which the alkali metal salt is potassium citrate.

18. A suppressant or method according to claim 17, in which the

potassium citrate is present in the concentration range 5 - 60 weight %.

19. A suppressant or method according to claim 18, in which the potassium citrate is present in the concentration range 40 - 60 weight %.

20. A suppressant or method according to any preceding claim, in which the surfactant has the structural formula RXM, where: M is a cation of an alkali metal (lithium, sodium, potassium, rubidium, caesium) or of a protonated amine; X is an anionic group; and R is an alkyl or alkylaryl group containing 4 to 20 carbon atoms.

21. A suppressant or method according to claim 20, in which the anionic group is taken from the group comprising a sulphate, a sulphonate and a carboxylate.

22. A suppressant or method according to claim 20 or 21, in which the alkyl group is a branched chain alkyl group.

23. A suppressant or method according to any one of claims 20 to 22, in which R contains at least one atom of silicon.

24. A suppressant or method according to claim 19 or 20, in which R contains the trimethylsilyl group $((\text{CH}_3)_3\text{Si}-)$.

25. A suppressant or method according to any one of claims 20 to 24, in which the molecular weight of the RX fragment is less than 400 Daltons.

26. A suppressant or method according to claim 25, in which the molecular weight of the RX fragment is less than 300 Daltons.

27. A suppressant or method according to any one of claims 20 to 26, in which the surfactant is present in the concentration in the range 0.1 to 2 weight %.

28. A suppressant or method according to claim 27, in which the surfactant is present in the concentration range 0.1 to 0.5 weight %.

29. A suppressant or method according to any preceding claim, in which the surfactant is a trimethylsilylbutane sulphate salt, $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-OSO}_3^-\text{M}'$, where M is an alkali metal cation selected from the group comprising sodium, potassium and a protonated amine.

30. A method according to any one of claims 2 to 29, in which the solution is dispersed to the fire or explosion in droplet sizes of less than $50\mu\text{m}$.

31. A method according to any one of claims 2 to 29, in which the solution is dispersed to the fire or explosion in droplet sizes of less than $100\mu\text{m}$.

32. A fire or explosion suppressant, substantially as described herein.

33. A method of suppressing a fire or explosion, substantially as described herein.

Fig.1.

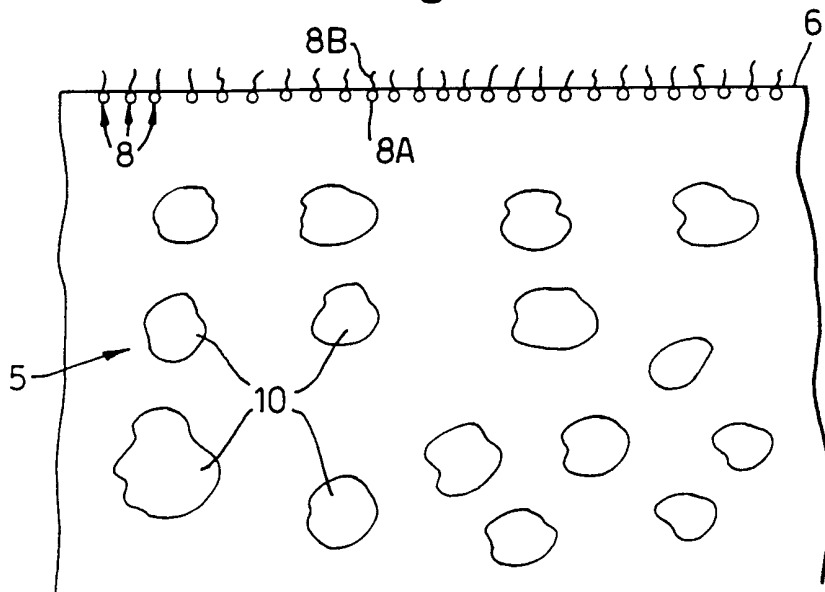


Fig.2.

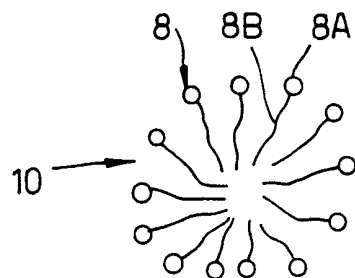


Fig.3.

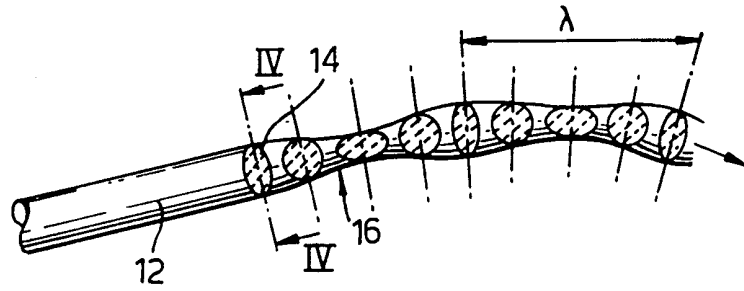
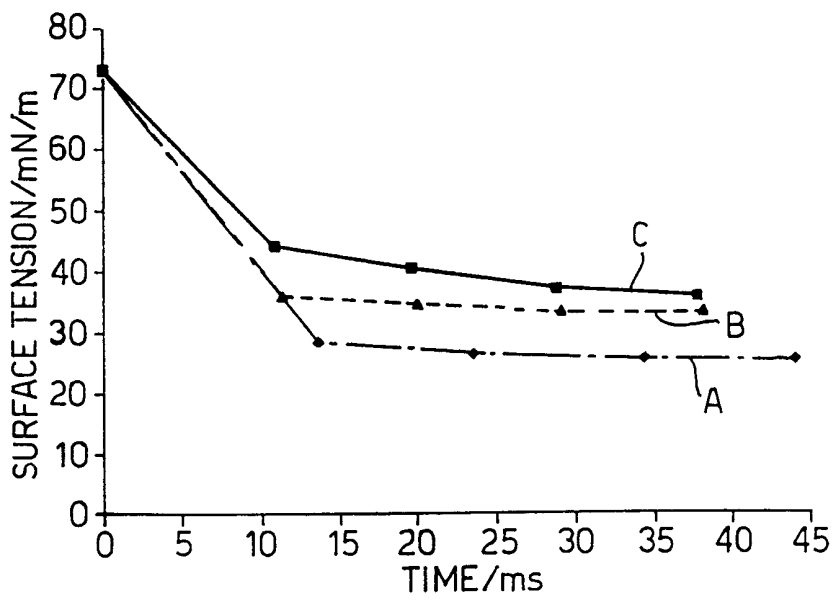


Fig.4.



Fig.5.



INTERNATIONAL SEARCH REPORT

Inter nal Application No PCT/GB 98/03360
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A62D1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A62D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 430 166 A (KLEIN KLAUS-DIETER ET AL) 4 July 1995 see column 3, line 40 - column 4, line 4	1-4, 20-33
Y	see column 7, line 13-41 see column 10; example 3 -----	22-29
X	WO 88 00482 A (TOJ PRODUKTIONS UND HANDELSGES) 28 January 1988	5-21
Y	see page 6, line 3-12; claims -----	22-29
X	FR 1 444 056 A (SOCIETE D'ETUDES CHIMIQUES POUR L'INDUSTRIE ET L'AGRICULTURE) 12 October 1966 see claims -----	5-10, 20, 21, 27

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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