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(54) Title: POLYCYANOACRYLATE FOAM (57) Abstract Polycyanoacrylate foam is made by mixing together a cyanoacrylate monomer, a liquid foaming agent and a polymerisa- tion initiator. The mixture simultaneously polymerises and foams. The foaming agent is usually an organic compound with a boil- ing point not higher than 100 °C, miscible with the monomer but not a solvent for the polymer. The monomer may be any 2-cya- noacrylate ester compatible with the composition.		

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POLYCYANOACRYLATE FOAM

This invention relates to a foam forming cyanoacrylate composition.

5

Since their commercialization in the sixties adhesives based on cyanoacrylate monomers have found wide application. Numerous compositions are known in the art. A variety of additional components are introduced into the cyanoacrylate monomer to impart thickening (US Patent No. 2,794,788) and thixotropy (US Patent No. 4,533,422) of the adhesive, toughness (WO 83/02,450), heat resistance (Japanese Patent No. 62,199,668), impact and peel-resistance (Japanese Patent No. 63,00,377), electroconductivity (WO 86/06,738) and other properties of the resultant adhesive bond.

15

It has now been unexpectedly found that when cyanoacrylate monomers are mixed with organic liquids and polymerization initiators the so formed composition can transform itself by simultaneous polymerization and expansion into a polycyanoacrylate foam.

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The present invention provides cyanoacrylate based composition, comprising a cyanoacrylate monomer, a liquid foaming agent and a cyanoacrylate polymerization initiator.

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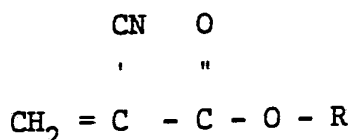
Upon or after formation of the composition it polymerizes to produce expanded polycyanoacrylate foam. The composition can also optionally contain other reactive monomers, as well as modifiers and additives such as polymeric thickeners, plasticizers, thixotropic agents, compatibilizers, pigments and colourants, fillers, deodorants and perfumes, for example.

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In another aspect the invention provides a method of creating a polycyanoacrylate foam and the foam itself.

5 The cyanoacrylate monomers used in the composition of the invention are 2-cyanoacrylate esters of the formula



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wherein R represents an ester-forming group. In principle, R can be any ester-forming group compatible with the monomer and with foam formation. For example, the group R should not initiate autopolymerization of the monomer or prevent
15 polymerization of the composition described above. R should also desirably be selected to provide a foam with the desired properties.

20 Preferably R represents alkyl, alkenyl, alkynyl, aryl or an aromatic heterocyclic radical. R may also be one of the foregoing moieties substituted with one or more other of the moieties; this includes the case of a substituent itself being substituted. Group R may contain other compatible substituents, for example alkoxy, alkoxyalkoxy,
25 carbalkoxyalkyl or halogen. In general, R can be any moiety which does not contain a sufficiently nucleophilic group to initiate polymerization or sufficiently electrophilic group to interfere with polymerization. The alkyl or alkenyl moiety may be cyclic and normally R contains from 1 to 16
30 carbon atoms and often is a 1C, 2C, 3C, 4C, 5C, 6C, 7C or 8C group, more usually it is a 1C-6C group. In the case of

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moieties containing a heterocycle, heteroatom ring members are normally counted as a carbon atom.

5 More preferably, R is alkyl, halogenated alkyl, alkenyl, alkynyl, phenyl, halogenated phenyl, phenylalkyl, halogenated phenylalkyl, alkoxyalkyl, alkoxyalkoxyalkyl, carbalkoxymethyl or alkylideneglyceryl, wherein the terms "alkyl" and "alkenyl" include the corresponding cyclic radicals. Uninterrupted carbon chains preferably contain 1,
10 2 or 3 carbon atoms.

Specific examples of R are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, trifluoroethyl, 2-chloroethyl, 3-chloropropyl,
15 2-chlorobutyl, cyclohexyl, tertiary butylcyclohexyl, benzyl, phenyl, cresyl, allyl, crotyl, methallyl, propargyl, furfuryl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxyisopropyl, 2-(2'-ethoxy)-ethoxymethyl, 2-(2'-ethoxy)-ethoxyethyl, 2-(2'-ethoxy)-ethoxybutyl, methoxycarbonylmethyl,
20 ethoxycarbonylmethyl, isopropoxycarbonylmethyl, isobutoxycarbonylmethyl, isoamylloxycarbonylmethyl and 1,2-isopropylideneglyceryl. Most preferred are ethyl, n-butyl, iso-butyl, 2-methoxyethyl, 2-ethoxyethyl and 2-methoxyisopropyl cyanoacrylates.

25 If desired, a mixture of two or more cyanoacrylate monomers may be used.

Usually the cyanoacrylate monomers are stabilized with
30 anionic and free-radical polymerization inhibitors. Anionic polymerization inhibitors known in the art are soluble acidic gases (for example sulfur dioxide), hydrogen fluoride, phosphonic, carboxylic and organic sulfonic acids,

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sultones, BF_3 and its complexes and phosphazenes, for example. The free-radical polymerization inhibitors are usually hydroquinone, p-methoxyphenol or t-butyl catechol, for example.

5

The inhibitors are normally used in small amounts of from 0.00001 to 1% by weight of the monomer. The preferred quantities for the above-mentioned inhibitors are: acidic gases - from 0.001% to 0.06%; acids - from 0.0005% to 0.01%;
10 sultones - from 0.01% to 0.1%; BF_3 - from 0.0001% to 0.01%; phosphazenes - from 0.0001% to 0.001%; free-radical inhibitors - from 0.001% to 1%. The foregoing percentages are percentages by weight of the cyanoacrylate monomer. It should be noted that the quantity of inhibitor will
15 influence the onset of polymerization of the composition of the present invention and could be used as a means to control the time interval between the formation of the composition and its transformation into a polymeric cyanoacrylate foam.

20

The liquid foaming agent used in the composition of the present invention can be any organic compound with a boiling point preferably not higher than 100°C. The liquid foaming agent used can be a single compound or a mixture
25 thereof. Preferably it will be soluble or semi-soluble in the cyanoacrylate monomer and will not act as a solvent for the corresponding polycyanoacrylate. Preferably its solubility parameter should be below 9. Preferably it is a non-polar liquid. Preferably it should be non-toxic,
30 non-flammable and non-irritant.

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Solubility parameter is a quantity used to predict the solubility of solutes and solvents and is explained in the "CRC Handbook of Chemistry and Physics", published by CRC Press Inc. of Boca Raton, Florida, USA see for example page 5 C-676 of the 67th Edition (1986-87). The CRC Handbook also contains lists of solubility parameter values.

Specific examples of foaming agents are pentane, hexane, heptane, 1,1,2-trichlorotrifluoroethane, 10 1,1,1-trichlorotrifluoroethane, petroleum ether, diethyl ether, cyclopentane, cyclohexane, benzene, carbon tetrachloride, chloroform, methylcyclopentane, dimethylsulfide, 1,1-dichloroethane, 1,1,1-trichloroethane, perfluorohexane, perfluoroheptane, 15 1-bromopropane. Most preferred are pentane, hexane, 1,1,2-trichlorotrifluoroethane, cyclohexane, petroleum ether and diethyl ether. The above-mentioned compounds are only representative and do not limit the compounds that can be used as liquid blowing agents. It was found that even very 20 polar liquids like ethanol and methanol or liquids which are typical solvents for polycyanoacrylates, like acetone, 2-butanone and acetonitrile, can be used as foaming agents.

When solvents for polycyanoacrylates are used as foaming 25 agents, they expand the foam but immediately thereafter the foam shrinks in volume or sometimes collapses. Such solvents are therefore normally unacceptable as foaming agents when used alone, but in principle can be used so long as the selected combination of solvent, polycyanoacrylate 30 and their relative quantities do not lead to collapse of the foam. Polycyanoacrylate solvents are more acceptable when used in minor amounts with other foaming agents.

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The volume ratio of cyanoacrylate monomer to foaming agent is not critical but is preferably from 1:10 to 20:1, more preferably from 1:2 to 5:1, especially from 1:1 to 4:1.

- 5 The cyanoacrylate polymerization initiator used in the composition of the present invention may comprise any of the known initiators and accelerators of the anionic polymerization of cyanoacrylate monomers, for example. The anionic initiator can be used singly or in admixture with
10 one or more other initiators.

Specific examples of anionic initiators are pyridine, aminopyridine, vinylpyridine, methoxyethylpyridine, piperidine, picoline, lutidine, N,N-dimethyl-p-toluidine,
15 N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, triphenylphosphine, triethylphosphine, tribenzylamine, triethylamine, benzyldimethylamine, diethylenetriamine, benzyltriethylamine, tribenzylamine, poly(4-vinylpyridine), calixarenes, tertiary amine-SO₃ complexes,
20 polyethyleneglycol, phenolformaldehyde resins, vinylimidazole, triethanolaminatotitanium, aminosilanes, phosphites, metal acetylacetonates, N-(oxydiethylene) benzothiazole-2-sulfenamide, bismuth dimethyldithiocarbamate, as well as alcohols, bases and
25 hydroxyl or amine group containing compounds. Most preferred anionic polymerization initiators are N,N-dimethyl-p-toluidine and N-(oxydiethylene) benzothiazole-2-sulfenamide.

- 30 The above-mentioned compounds are only representative and do not restrict the scope of suitable initiators. For example any of the anionic polymerization initiators known in the

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art for cyanoacrylate monomers or accelerators of their anionic polymerization can successfully be used in the compositions of the present invention. Optionally, but not necessarily, free-radical polymerization initiators such as

5 methylethylketone peroxide, cyclohexane peroxide, cumene hydroperoxide or dibenzoyl peroxide, for example, can be used in conjunction with the anionic polymerization initiator.

10 In order to impart desired properties to the composition of the present invention and to the properties of the resultant foam, as well as for economic considerations, further additives can be introduced into the composition. They can be, for example, any of the known polymeric thickeners and

15 viscosity regulators, rubbers, plasticizers and tougheners, compatibilizers, thioxotropic agents, colourants, deodorants or perfumes, for example, used in cyanoacrylate adhesives.

The composition may also contain other monomers containing a

20 reactive double bond, for example (di)acrylates or (di)methacrylates, or reactive resins or oligomers, e.g. epoxy or urethane, in minor amounts, e.g. up to 25 mole % of the total monomer content and more preferably in an amount of no more than 5 or 10 mole %.

25 Upon mixing the three major components of the present invention (monomer, foaming agent and initiator) a mixture is formed in which, under the action of the anionic initiator, polymerization of the cyanoacrylate monomer

30 occurs. It is fast and exothermic, which leads to the simultaneous evaporation of the liquid foaming agent. As a result polycyanoacrylate foam is produced. The expanded material can occupy a volume of as much as 40 times the

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volume of the original liquid composition. The expansion coefficient and the properties of the foam are dependent on the components used and their ratios. They are also dependent on the available volume for expansion. The
5 formed polymeric foam is of a closed-cell type.

A distinctive feature is that the foam is covered by a thin film of polycyanoacrylate, which resembles a polycyanoacrylate glue-line and ensures excellent adhesion
10 of the foam to the surface(s) which it has contacted. The time necessary for the onset of polymerization and foaming can be regulated from seconds to minutes by varying the type and amount of anionic initiator and/or stabilizer present in the cyanoacrylate monomer or composition.

15 Another distinctive feature of the composition of the present invention is that it is easy to prepare, the foaming reaction takes place at room temperature and compressed gases are not required or utilized.

20 Another distinctive feature of the foamed polycyanoacrylate is that it can easily be collapsed when contacted with solvents for polycyanoacrylates like acetone, acetonitrile, methylenechloride, N,N-dimethylformamide, nitromethane,
25 butyrolactone or alkyl cyanoacetates, for example.

Applications of the foaming composition of the present invention and the method of obtaining polycyanoacrylate foams include two major areas, i.e. plugging of ducts,
30 pipes and vessels and, secondly, adhesive bonding and sealing of porous substrates.

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Using the foaming composition of the present invention temporary, permanent or semi-permanent blocking of flow of fluids in pipelines can be achieved. Gas and oil pipelines are of particular interest. Following repairs or other work
5 on the pipeline the foam blockage can easily be collapsed by application of a suitable solvent. The main advantage of the material and method of the invention is the simplicity and speed of forming the foam, its high adhesion to the walls of the pipe, and the simplicity and speed of
10 collapsing the foam.

Using the foaming composition of the present invention blood vessel occlusion, fallopian tube sealing or other medical or surgical procedures can be achieved. The above-mentioned
15 applications are currently executed with conventional cyanoacrylates for the purpose of stopping haemorrhage and for female sterilization. Using the foaming composition in those cases would greatly increase the success rate of the present methods, ensuring excellent plugging capacity as a
20 result of polymer expansion in the vessel. Furthermore the quantity of the cyanoacrylate introduced into the body will be reduced more than tenfold, which would greatly increase the physiological safety of the procedures.

25 Using the foaming composition of the present invention orthopaedic casts for broken limbs can be prepared. The distinct advantages will be the speed and ease of preparation of the casts, their extremely low weight and sufficient rigidity, advantages specially valuable in
30 emergency cases and military action.

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5 The cyanoacrylate monomer and the initiator must obviously be kept separate until it is desired to form the foaming composition, but the foaming agent may if desired be mixed with one or other (or both) of the monomer and the initiator to form a preblend.

10 It is therefore convenient to provide a binary delivery system holding the monomer and the initiator in separate containers from which they may be dispensed and mixed. If desired, the binary system could include a third container containing all or part of the foaming agent, and if desired separate containers holding other components may be provided. Such a binary or multipart delivery system forms one aspect of the invention.

15 The delivery system or kit may take the form of a syringe having an in-line static (stationary phase) mixer or of spray apparatus. In any event, it preferably includes means to mix the components prior to, or in the process of, their
20 dispensing from the apparatus. In the case of a syringe, a thickener is preferably provided to increase the viscosity of the final composition.

25 Preferably, the delivery system is a two-part system, in which all the components are included in the containers holding the monomer preparation and the initiator.

The invention includes a preblend for forming the foaming composition, comprising the monomer and a foaming agent.

30 The above-mentioned applications are only indicative and do not limit the scope or application of the foaming composition of the present invention.

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The invention is illustrated by the following examples.

Example 1

5 In an open polyethylene cylindrical container with a diameter of 50 mm, 4 ml of pure, freshly distilled ethyl 2-cyanoacrylate are placed. To the cyanoacrylate is added a given amount of liquid foaming agent, containing N,N-dimethyl-p-toluidine. The contents are manually mixed
10 for 3 seconds so that a clear solution is produced. The so formed composition is left static and the time lapse before the onset of expansion and the time interval of actual expansion is recorded. The volume of the expanded foam is measured and the coefficient of expansion is calculated as
15 the ratio of the volume of the polycyanoacrylate foam to the volume of the cyanoacrylate monomer in the composition. The results are shown in Table 1.

20 In Table 1, the concentration of initiator is expressed as percentage by weight based on the total composition.

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Table 1

Foaming compositions based on different foaming agents (FA)

Foaming agent	Volume ratio of cyanoacrylate to FA	Concentr. of initiator	Solubility parameter of FA	Polarity of FA	b.p. of FA	Onset time	Time of expansion	Expansion coefficient
		wt. %			°C	sec	sec	
Pentane	1:1	0.025	7.0	non	35	20	5	23
Hexane	2:1	0.017	7.3	non	69	25	5	13
1,1,2-tri-chlorotri-fluoroethane	4:1	0.010	7.3	non	48	6	6	25
Heptane	4:1	0.020	7.4	non	98	10	10	4
Diethyl ether	4:1	0.010	7.4	mod	35	19	5	18
Cyclohexane	2:1	0.017	8.2	non	81	34	5	10
2-Butanone	2:1	0.017	9.3	mod	80	10	15	17
Acetone	2:1	0.017	9.9	mod	56	5	10	22 *
Ethanol	2:1	0.017	10.0	high	78	5	10	10
Acetoni-trile	2:1	0.017	11.9	high	82	10	10	3
Methanol	4:1	0.020	14.5	high	65	5	25	8

*Foam collapses after expansion

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The ratio of ethyl 2-cyanoacrylate monomer to foaming agent in Table 1 was established to be the best for each pair in previous experiments. The results indicate that the most important factor in choosing the foaming agent is its boiling point and as can be seen the lower the boiling point the higher is the expansion which can be achieved. The following major consideration is the polarity and the solubility parameter of the foaming agent. Best results are produced with non-polar solvents with solubility parameters at the lower end of the scale, e.g. pentane, 1,1,2-trichlorotrifluoroethane. Foaming agents with solubility parameters at the other end of the scale and high polarity are normally unsuitable due to the formation of exceptionally brittle foams. Foaming agents with a solubility parameter similar to poly(ethyl 2-cyanoacrylate) and thus being good solvents for the foam, e.g. acetone, are also unsatisfactory due to immediate shrinkage and collapse of the foamed material. Solvents in the mid-range of the solubility parameter scale and with boiling point around 80°C, like cyclohexanone, produce resilient foams.

Example 2

Experiments according to the procedure described in Example 1 were carried out. Ethyl 2-cyanoacrylate was used as the cyanoacrylate monomer and 1,1,2-trichlorotrifluoroethane as the foaming agent. Different anionic polymerization initiators were evaluated. The ratio of cyanoacrylate to 1,1,2-trichlorotrifluoroethane and the concentration levels of the initiators were optimized in previous experiments. The results are presented in Table 2.

Table 2

Foaming compositions based on different anionic polymerization initiators (API)

API	Concentration of API in composition	Volume ratio of cyanoacry- late to foam- ing agent	Onset time	Time of expan- sion	Expansion coefficient
wt. %					
			sec	sec	
N,N-Dimethyl- p-toluidine	0.010	4:1	6	6	25
Pyridine	0.0002	4:3	450	20	5
Piperidine	0.010	2:1	30	10	18
Triethyl phosphine	0.003	2:1	133	40	17
Triphenyl phosphine	0.0048	4:3	298	68	4
N-(oxydiethylene) benzothiazole-2- sulfenamide	0.017	2:1	25	5	25

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The results summarized in Table 2 show that best expansion coefficients and time of expansion are achieved with N,N-dimethyl-p-toluidine and N-(oxydiethylene)benzothiazole-2-sulfenamide, the latter having the advantage of no odour. Piperidine gives slightly longer onset times and is very smelly. Very slow onset and expansion times can be achieved with triethylphosphine and triphenylphosphine.

Example 3.

Experiments according to the procedure described in Example 1 were carried out. Ethyl 2-cyanoacrylate was used as the cyanoacrylate monomer. 1,1,2-Trichlorotrifluoroethane was used as foaming agent. Their ratio was 4:1 by volume. N,N-dimethyl-p-toluidine was used as initiator in 0.01% by weight of the composition. The cyanoacrylate monomer was stabilized with p-toluenesulfonic acid or trifluoromethanesulfonic acid. The results of the onset time of foaming are presented in Table 3.

Table 3Stabilized foaming compositions

Acid	Concentration of acid in cyanoacrylate wt. %	Onset time sec
p-Toluenesulfonic	0	10
p-Toluenesulfonic	0.0003	14
p-Toluenesulfonic	0.0006	16
p-Toluenesulfonic	0.0012	20
p-Toluenesulfonic	0.002	37
p-Toluenesulfonic	0.005	66
p-Toluenesulfonic	0.01	195
Trifluoro- methanesulfonic	0	10
Trifluoro- methanesulfonic	0.001	11
Trifluoro- methanesulfonic	0.002	24
Trifluoro- methanesulfonic	0.005	43
Trifluoro- methanesulfonic	0.01	117

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The results presented in Table 3 clearly demonstrate that the introduction of sulfonic acids, which are often used commercially to stabilize the cyanoacrylate monomers, can increase the onset time of foam expansion and by regulating their level the period between mixing the composition of the present invention and its expansion into polymer foam can be controlled.

Example 4

Experiments according to the procedure described in Example 1 were carried out. Different types of cyanoacrylate monomers were used. 1,1,2-Trichlorotrifluoroethane was used as foaming agent. N,N-dimethyl-p-toluidine was used as initiator in amount of 0.01% by weight of the composition. The expansion coefficient data are shown in Table 4.

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Table 4Foaming compositions based on different cyanoacrylate monomers

Cyanoacrylate monomer	Volume ratio of cyanoacrylate to foaming agent	Expansion coefficient
Methyl 2-cyanoacrylate	4:1	13
Ethyl 2-cyanoacrylate	4:1	25
Butyl 2-cyanoacrylate	1:1	29
iso-Butyl 2-cyanoacrylate	1:1	35
Allyl 2-cyanoacrylate	1:1	20
2-Methoxyethyl 2-cyanoacrylate	4:3	20
2-Ethoxyethyl 2-cyanoacrylate	4:3	15
2-Methoxyisopropyl 2-cyanoacrylate	4:3	23

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Example 5

Compositions based on various cyanoacrylate monomers and 1,1,2-trichlorotrifluoroethane in a volume ratio of 4:1 and containing 0.01% by weight N,N-dimethyl-p-toluidine as initiator were injected into polyethylene tubes with an internal diameter of 12.5 mm. Seconds after the injection, the composition expanded into polycyanoacrylate foam which plugged the tubes. The walls of the tubes were carefully cut and the foamed material removed. Test pieces of the foam were cut from it and tested. The results of some physical characteristics of the foams are presented in Table 5.

Table 5Physical characteristics of polycyanoacrylate foams

2-Cyano- acrylate monomer	Specific gravity g/cm ³	Tensile strength at break kg/cm ²	Elonga- tion at break %	Tensile shear strength at break kg/cm ²	Compression strength at 10% deforma- tion kg/cm ²
Methyl	0.28	0.8	2.5	0.5	5.7
Ethyl	0.13	10.6	3.7	5.2	4.9
Butyl	0.25	5.7	6.7	1.8	4.9
iso-Butyl	0.24	3.2	3.7	3.0	5.7
Allyl	0.18	5.0	3.0	3.0	7.3
2-Methoxy- ethyl	0.41	1.6	2.0	1.9	6.5
2-Ethoxy- ethyl	0.22	1.6	1.7	1.5	5.5
2-Methoxy- isopropyl	0.28	1.8	2.0	1.7	4.0

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Example 6

5 Tubes and pipes made of cast iron, stainless steel, copper, polycarbonate, polystyrene, polyvinylchloride, polypropylene and polyethylene having inside diameters from 1 mm to 100 mm were plugged with foam by injecting through a specially drilled opening a foaming composition consisting of ethyl 2 cyanoacrylate and 1,1,2-trichlorotrifluoroethane in a volume ratio of 4:1 and containing 0.01% by weight

10 N,N-dimethyl-p-toluidine. The expanded foam created an efficient plug, whose adhesion to the pipe wall was higher than the strength of the foam material itself. The pipes were hermetically sealed by the foam plug and easily withstood pressure of 10 Atmospheres.

15

In a following operation acetone was injected with a syringe through the same opening used for injecting the composition, which subsequently was also plugged with foam. In 5 seconds to 2 minutes, depending on the size of the pipe, the foam

20 collapsed and flow through the pipe was restored.

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CLAIMS

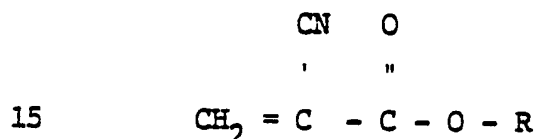
1. A foam-forming cyanoacrylate composition comprising a
2-cyanoacrylate ester monomer, a liquid foaming agent and a
polymerization initiator, for anionic polymerization of the
monomer, which composition upon or after mixing polymerizes
and foams to produce a polycyanoacrylate foam.
2. A composition as claimed in claim 1, wherein the
cyanoacrylate monomer and the liquid foaming agent are in a
volume ratio from 1:10 to 20:1.
3. A composition as claimed in claim 1 or claim 2, wherein
the polymerization initiator is in an amount of from
0.00001% to 1% by weight of the composition.
4. A composition as claimed in any one of the preceding
claims, wherein the foaming agent is an organic compound
with a boiling point not higher than 100°C.
5. A composition as claimed in claim 4, wherein the foaming
agent is miscible with the cyanoacrylate monomer.
6. A composition as claimed in claim 5, wherein the foaming
agent has a solubility parameter below 9 and is non-polar.
7. A composition as claimed in claim 4, wherein the foaming
agent is pentane, hexane, heptane,
1,1,2-trichlorotrifluoroethane,
1,1,1-trichlorotrifluoroethane, petroleum ether, diethyl
ether, cyclopentane, cyclohexane, benzene, carbon
tetrachloride, chloroform, methylcyclopentane,
dimethylsulfide, 1,1-dichloroethane, 1,1,1-trichloroethane,

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perfluorohexane, perfluoroheptane, 1-bromopropane or a mixture thereof.

8. A composition as claimed in claim 7, wherein the foaming agent is pentane, hexane, 1,1,2-trichlorotrifluoroethane, petroleum ether, cyclohexane or diethyl ether or is a mixture thereof.

9. A composition as claimed in any one of the preceding claims, wherein the cyanoacrylate monomer comprises one or more compounds of the formula



wherein R is alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl or an aromatic heterocyclic radical or is one of these moieties substituted with one or more other of the moieties, and wherein these moieties may optionally be substituted with alkoxy, carbalkoxyalkyl, halogen or another inert substituent.

10. A composition as claimed in claim 9, wherein R contains from 1 to 16 carbon atoms, the heteroatom ring members of any aromatic heterocycle being counted as a carbon atom.

11. A composition as claimed in claim 9 or claim 10, wherein R is alkyl, halogenated alkyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, alkenyl, alkynyl, phenyl, halogenated phenyl, phenylalkyl, halogenated phenylalkyl,

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alkylphenyl, halogenated alkylphenyl, alkylphenylalkyl,
halogenated alkylphenylalkyl, alkoxyalkyl,
alkoxyalkoxyalkyl, carbalkoxymethyl or
isopropylideneglyceryl.

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12. A composition as claimed in claim 11, wherein R is ethyl, n-butyl, iso-butyl, 2-methoxyethyl, 2-ethoxyethyl or 2-methoxyisopropyl.

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13. A composition as claimed in any one of the preceding claims, wherein the initiator is pyridine, aminopyridine, vinylpyridine, methoxyethylpyridine, piperidine, picoline, lutidine, N,N-dimethyl-p-toluidine,

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N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, triphenylphosphine, triethylphosphine, tribenzylamine, triethylamine, benzyldimethylamine, diethylenetriamine, benzyltriethylamine, tribenzylamine, poly(4-vinylpyridine), a calixarene, a tertiary amine-SO₃ complex,

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polyethyleneglycol, a phenolformaldehyde resin, vinylimidazole, triethanolaminatotitanium, an aminosilane, a phosphite, a metal acetylacetonate, N-(oxydiethylene) benzothiazole-2-sulfenamide, bismuth dimethyldithiocarbamate, an alcohol, a base or a hydroxyl or amine group containing compound.

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14. A composition as claimed in claim 13, wherein the initiator is N,N-dimethyl-p-toluidine or N-(oxydiethylene) benzothiazole-2-sulfenamide.

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15. A composition as claimed in any one of the preceding claims and which further comprises a free-radical polymerization inhibitor or an anionic polymerization

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inhibitor in an amount insufficient to inhibit the initiator, or both.

16. A composition as claimed in any one of the preceding
5 claims and further comprising another reactive monomer or a reactive resin or oligomer, a thickener, a viscosity regulator, a rubber, a plasticizer, a toughener, a compatibilizer, a thixotropic agent, a colourant, a deodorant or a mixture thereof.

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17. A poly(2-cyanoacrylate ester) foam, the polymer
15 optionally including a minor amount of one or more other monomer units than 2-cyanoacrylate ester units or a reactive resin or oligomer.

18. A foam as claimed in claim 17, wherein the
20 2-cyanoacrylate ester is as defined in any one of claims 9 to 12.

19. A method of forming a poly(2-cyanoacrylate ester) foam,
comprising forming a composition as defined in any one of
25 claims 1 to 16 and allowing the monomer to polymerize and form a foam.

20. A method as claimed in claim 19 wherein the components
of the composition are mixed together in a static mixer or
in a spray.

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21. A kit or device for forming a poly(2-cyanoacrylate
ester) foam, comprising a first container containing
2-cyanoacrylate ester monomer and a second container

- 26 -

5 containing a polymerization initiator for anionic polymerization, the kit additionally containing a liquid foaming agent in the first container, in the second container or in a third container or in any combination thereof.

10 22. A kit or device as claimed in claim 21, wherein the monomer is as defined in any one of claims 9 to 12, the foaming agent is as defined in any one of claims 4 to 8, the initiator is as defined in claim 13 or claim 14, the monomer and the foaming agent are in a volume ratio of from 1:10 to 20:1, and/or the polymerization initiator is in an amount of from 0.00001% to 1% by weight of the total contents of the kit.

15 23. A kit or device as claimed in claim 21 or claim 22 wherein the monomer is in admixture with an anionic polymerization inhibitor or a free radical polymerization inhibitor or both, and/or one or more of the containers additionally contains one or more of the further components defined in claim 16.

20 24. A kit or device as claimed in any one of claims 21 to 23 which comprises a two part or three part syringe.

25 25. A kit or device as claimed in any one of claims 21 to 23 wherein the first and second containers and any third container are connected by ducts to a spray head for mixing the contents of the containers and means is provided to expel the contents of the containers through the ducts to the spray head.

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- 27 -

26. A delivery system for forming a composition as defined in any one of claims 1 to 16 the system comprising the monomer and the initiator in separate containers from which they may be dispensed, the foaming agent being included in said containers and/or in a separate container, and the system optionally including means to mix the container contents before or as they are dispensed from the system.

27. A preblend for forming a cyanoacrylate foam, comprising a 2-cyanoacrylate ester monomer and a liquid foaming agent.

28. A preblend as claimed in claim 27, wherein the cyanoacrylate monomer and the foaming agent are in a volume ratio of from 1:10 to 20:1, the foaming agent is as defined in any one of claims 4 to 8 and/or the cyanoacrylate monomer is as defined in any one of claims 9 to 12.

29. A preblend as claimed in claim 27 or claim 28 and which further comprises a free-radical polymerization inhibitor, an anionic polymerization inhibitor or both, and/or one or more further components as defined in claim 16.

30. A method of blocking a pipe, comprising placing in the pipe a composition as defined in any one of claims 1 to 16 and allowing the composition to polymerize to form a foam which blocks the pipe.

31. A method as claimed in claim 30, wherein the pipe is blocked temporarily and is subsequently unblocked by applying to the foam a solvent therefor.

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32. A method of forming a cast, for example for a broken or injured limb, comprising applying a composition as defined in any one of claims 1 to 16 to the limb or other body around which the cast is to be formed and allowing the composition to polymerize and foam to form a cast.

33. A method of occluding or stopping a blood vessel, fallopian tube or other tubular part of a human or animal body, comprising applying to the tubular part a composition as defined in any one of claims 1 to 16 and allowing the composition to polymerize to form a foam occluding to stopping the tubular part.

34. The use of 2-cyanoacrylate ester monomer as a starting material to form a polycyanoacrylate foam.

35. The use of claim 34, wherein the monomer is as defined in any one of claims 9 to 12.

36. The use of an organic liquid with a boiling point of no greater than 100°C as a foaming agent to form a polycyanoacrylate foam.

37. The use of claim 36, wherein the organic liquid is as further defined in any one of claims 6 to 8.

38. A composition as defined in any one of claims 1 to 16 for use in the treatment of the human or animal body by surgery or therapy.

39. A method of forming a polymer foam on or around a part of the human or animal body, comprising applying a composition as defined in any one of claims 1 to 16 on or around the part.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/02121

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 C 08 J 9/14 // A 61 L 15/12 C 08 L 35:04

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl.5	C 08 J A 61 L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,P	Chemical Abstracts, vol. 115, no. 6, 12 August 1991, (Columbus, Ohio, US), see abstract no. 51548k, & JP,A,3091542 (TORAY INDUSTRIES) 17 April 1991, see abstract ---	1-12,16 -20,27- 31,34- 39
Y	---	21-26
Y	DE,A,3421360 (REICH SPEZIALMASCHINEN GmbH) 12 December 1985, see claims 1-3	1-31,34 -39
Y	---	21-26
A	FR,A,2359170 (POLYMERICS INC.) 17 February 1978, see claims 1-2 ---	1-31,34 -39
A	FR,A,2610828 (MOSKOVSKY GOSUDARSTVENNY MEDITSINSKY INSTITUT) 19 August 1988, see claims 1-3 ---	1-31,34 -39
	-/-	

¹⁰ Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

06-03-1992

Date of Mailing of this International Search Report

09. 04. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

[Signature] A. TORIBIO

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>Chemical Abstracts, vol. 100, no. 18, (Columbus, Ohio, US), J.A. NIGHTINGALE et al.: "Use of methyl cyanoacrylate (MCA) as a sclerosing agent in female sterilization: effect of inhibitors and radiopaque additives on MCA polymerization in vitro and on oviduct occlusion in vivo in rabbits", see abstract no. 144952t, & POLYM. PREPR. (AM. CHEM. SOC., DIV. POLYM. CHEM.), 24(1), 28-9, see abstract -----</p>	1-31, 34 -39

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATION WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This International search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claim numbers 32, 33 because they relate to subject matter not required to be searched by this Authority, namely:
see PCT-Rule 39.1(iv)
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this International application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the International application
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the International application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9102121

SA 53834

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 25/03/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A- 3421360	12-12-85	None	
FR-A- 2359170	17-02-78	US-A- 4094685	13-06-78
		DE-A- 2733040	09-02-78
		GB-A- 1589022	07-05-81
		JP-A- 53034863	31-03-78
FR-A- 2610828	19-08-88	None	