

(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 199722938 B2**
(10) Patent No. **719265**

(54) Title
Neutral removers of paint from essentially metallic surfaces

(51)⁶ International Patent Classification(s)
C09D 009/00

(21) Application No: **199722938**

(22) Application Date: **1997 .04 .02**

(87) WIPO No: **WO97/38057**

(30) Priority Data

(31) Number	(32) Date	(33) Country
MI96A000673	1996 .04 .05	IT

(43) Publication Date : **1997 .10 .29**

(43) Publication Journal Date : **1998 .01 .08**

(44) Accepted Journal Date : **2000 .05 .04**

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OPI DATE 29/10/97 APPLN. ID 22938/97
AOJP DATE 08/01/98 PCT NUMBER PCT/EP97/01654



AU9722938

PCT)

(51) International Patent Classification ⁶ : C09D 9/00		A1	(11) International Publication Number: WO 97/38057
			(43) International Publication Date: 16 October 1997 (16.10.97)
(21) International Application Number: PCT/EP97/01654		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 2 April 1997 (02.04.97)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: MI96A000673 5 April 1996 (05.04.96) IT			
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(54) Title: NEUTRAL REMOVERS OF PAINT FROM ESSENTIALLY METALLIC SURFACES			
(57) Abstract Compositions capable of removing resinous coatings from essentially metallic surfaces, containing hydrogen peroxide and gamma-butyrolactone, and being characterized by the presence of benzyl alcohol as main organic solvent, the content of said gamma-butyrolactone being lower than or equal to 20 % by wt. of the total weight of said compositions.			

NEUTRAL REMOVERS OF PAINT FROM ESSENTIALLY METALLIC SURFACES

Field of the invention

The present invention relates to neutral compositions capable of removing resinous coatings from essentially metallic substrates.

5 State of the art

As paints based on catalysed epoxy and polyurethane resins, containing heavy metals, and paint primers containing chromates, phosphates and other inhibitory pigments are used to coat aircraft's metallic surfaces, there is a need for suitable paint removers capable of
10 thoroughly eliminating said paints from the aircraft being overhauled, without corroding their metallic surface.

The acid-based paint removers available eliminate said coatings effectively, but can corrode the metallic surface of the substrate.

Also basic paint removers based on ammonia were used, but proved to be
15 ineffective for said paints.

The best state-of-the-art removers of paints consisting of epoxy and polyurethane resins are based on methylene chloride. However, said solvent, which is highly volatile, creates serious pollution problems especially when used for paint removal from large-sized metallic
20 surfaces, as aircraft's. Furthermore, it is suspected of being carcinogenic.

Finally, methylene chloride is very fast acting but, due to its volatility, exerts an action of short duration. It follows that, when a thick paint layer is to be removed, repeated applications are
25 necessary.

To overcome the aforementioned disadvantages inherent in the use of

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methylene chloride, paint removers with methylene chloride replaced partly or completely by N-alkylpyrrolidone have been proposed. However, said solvents exhibit a much reduced paint removing action since they contain hydrogen lactam which forms hydrogen bonds with water.

USP 3,355,385 discloses that ketones, such as acetone and methylethylketone, combined with peroxides, exhibit an adequate paint removing action. However, also these solvents, like methylene chloride, are highly volatile and, consequently, little effective.

Therefore, the need for paint removers not having the disadvantages of the removers of the prior art and, at the same time, not arousing serious problems of environmental impact and, furthermore, being biodegradable, is deeply felt.

International patent application WO 93/18865 discloses a neutral paint removing composition containing hydrogen peroxide and a water-soluble solvent consisting of a short-chain acid ester, such as gamma-butyrolactone.

As gamma-butyrolactone is rather expensive, with a view to reducing the cost of said composition, the aforementioned patent application envisages the use of a second solvent selected from alkylene glycols, alcohols, such as for example cyclohexanol, tetrahydrofurfuryl alcohol, substituted lactams, such as N-methylpyrrolidone, as well as specific hydrocarbons.

According to the aforesaid patent application, the gamma-butyrolactone content must equal at least 25% and the cosolvent content, if any, must be lower than 20%; otherwise the paint removing action of the relevant composition will be low.

The present invention

The Applicant has now found compositions capable of completely removing resinous coatings from essentially metallic substrates, containing hydrogen peroxide and gamma-butyrolactone and being characterized by the presence of benzyl alcohol at a concentration greater than or equal to that of gamma-butyrolactone, the concentration of said gamma-butyrolactone being lower than or equal to 20% by wt. of the total weight of said compositions.

In particular, the compositions of the present invention comprise:

- a) 5% to 30% by wt. hydrogen peroxide;
- b) 20% to 50% by wt. water;
- c) 5% to 20% by wt. gamma-butyrolactone;
- d) 20% to 50% by wt. benzyl alcohol.

Furthermore, the compositions being the object of the present invention are non-corrosive, biodegradable, and, thanks to their high flash point (approx. 100°C) may be handled in an easy way.

Also, this invention extends to the use of said compositions to remove primers and finishes consisting of polyurethane and epoxidic paints from large-sized metallic surfaces, like aircraft's, which in particular are constructed of aluminium alloys.

The claimed compositions can also remove acrylic and vinyl paints.

Detailed description of the invention

The compositions of the invention may optionally contain at least one of the following types of additives, such as for example corrosion inhibitors, thickeners, surfactants, and colouring agents.

The compositions of the present invention preferably contain at least one of the following thickeners: cellulosic derivatives (such as hydroxypropyl cellulose, ethylcellulose, methylcellulose), pyrogenic



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amorphous silica treated for water repellency, at least one polyacrylamide dispersion in mineral oil, aqueous dispersions of acrylic polymers, and aqueous emulsions of non-ionogenic polyurethanes.

5 According to a particularly preferred embodiment of the present invention, the compositions contain a mixture of the following components: cellulosic derivatives, silica, and aqueous dispersions of acrylic polymers or aqueous suspensions of non-ionogenic polyurethanes.

10 In this specific case, the cellulosic derivative used is hydroxypropyl cellulose having an average molecular weight of 100,000 to 1,200,000, available under the trademark KLUCEL[®], in concentrations ranging from 0.1 to 3% by wt., the acrylic polymers aqueous dispersions preferably used are those available under the trademark RHEOLATE[®], the
15 polyurethane aqueous emulsions preferably used are those available under the trademark REOX[®]; the concentration of said acrylic polymers aqueous dispersions or of said polyurethanes aqueous emulsions shall not exceed 5%.

The quantity of silica added as a thickener and as antidripping
20 agent ranges from 0.1% to 2% of the total weight of the composition. The aforesaid acrylic polymers aqueous dispersions and polyurethanes aqueous emulsions may be replaced by two different types of polyacrylamide dispersions in mineral oil, available under the trademarks VISCALEX[®] and COLLAFIX[®], respectively, the total
25 concentration of said dispersions having to range from 1% to 5% by wt. of the total weight of the composition.

The claimed compositions contain at least one of the following

corrosion inhibitors: butynediol hydroxyethylethers, gallic and metadigallic acid glycosidic esters, calcium silicate, sodium polyphosphate, thiourea in propargyl alcohol in a concentration of 50%, and the metallic phosphates generally used in paints.

5 According to a preferred embodiment of the present invention, the compositions contain: 1,4-bis(2-hydroxyethoxy)-2-butyne, available under the trademark BUTYNE[®] 497, sodium polyphosphate, thiourea in propargyl alcohol, available under the trademark ARMOHIB[®], and calcium silicate, available under the trademark SHIELDEX[®], the total
10 amount of each corrosion inhibitor having to range from 2% to 10%.

According to particularly preferred embodiments of the present invention, the compositions contain the following corrosion inhibitors: zinc phosphate activated with zinc molybdate, available under the trademark ACTIROX[®], zinc phosphate modified with organic
15 components, available under the trademark HEUCOPHOS[®], or mixtures thereof, and optionally the aforementioned 1,4-bis(2-hydroxyethoxy)-2-butyne, available under the trademark BUTYNE[®] 497; the total concentration of said corrosion inhibitors in the final composition shall not exceed 15% by wt.

20 The use of the aforesaid corrosion inhibitors implies the use of metallic borates having the function to activate said corrosion inhibitors. The following borates, in concentrations of 10% by wt. max., are preferably used: modified barium metaborate, available under the trademark BUTROL[®] and zinc borate.

25 The claimed compositions preferably contain at least one of the following surfactants: N-alkyl-pyrrolidone, in which the alkyl group contains 8 to 18 carbon atoms, and sodium

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caprylamphohydroxypropylsulphonate.

According to a particularly preferred embodiment of the present invention, the compositions contain a mixture of N-dodecylpyrrolidone, available under the trademark SURFADONE[®], and sodium caprylamphohydroxypropylsulphonate, available under the trademark MIRANOL[®], the total concentration of said surfactants having to range from 1% to 5% of the total weight of said compositions.

The claimed compositions may optionally contain small amounts of colourant, preferably a pigment based on iron oxides in water, in a concentration of 0.01% to 0.1%.

The compositions of the present invention are preferably formulated in the form of two separate components, A and B, which may be mixed immediately prior to use, wherein component A contains benzyl alcohol, gamma-butyrolactone and optionally at least one of the additives mentioned above, and component B consists of a 35% aqueous solution of hydrogen peroxide.

The Applicant has found that the composition of the invention formulated in the two-component form is an effective paint remover for a long time, actually for 6 to 12 months.

Components A and B will be so formulated that benzyl alcohol, gamma-butyrolactone, water, and hydrogen peroxide concentrations in the final compositions of the invention are within the aforementioned ranges.

It is a further object of the present invention to provide a process for the application of the claimed two-component compositions consisting of the following steps:

i) components A and B, in weight ratios ranging from 100:50 to 100:30,

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preferably 100:40, are fed through separate suction pumps to an appropriate mixer where mixing of the two components takes place;

ii) the resulting composition is applied by spray gun to the substrate wherefrom the paint is to be removed.

5 The compositions of the present invention are to remain on the films of paint until they are completely detached from the supports. Washing with a jet of water is enough to eliminate both paint and paint removing compositions, while brushes or similar tools may be used to remove resinous residues, if any.

10 The following examples relating to the preparation and application of a particularly preferred composition of the invention as well as the paint removing tests conducted on said composition are reported below by way of indication, not of limitation, of the present invention.

EXAMPLE 1

Preparation of component A

		Parts by wt.
	1) benzyl alcohol	573
5	2) gamma-butyrolactone	244
	3) KLUCEL [®] (hydroxypropyl cellulose)	14
	4) BUTYNE 497 [®] (1,4-bis(2-hydroxyethoxy)-2-butyne)	22
10	5) ARMOHIB 18 [®] (thiourea in propargyl alcohol)	20
	6) MIRANOL JS [®] (caprylamphohydroxypropylsulphonate)	30
	7) SURFADONE LP-300 [®] (N-dodecyl-pyrrolidone)	10
15	8) water	20
	9) sodium polyphosphate	10
	10) RED AW 305 [®] (water iron oxide)	1
20	11) SHIELDEX AC 5 [®] (calcium silicate)	20
	12) CAB-O-SIL TS 720 [®] (water repellent amorphous silica)	8
	13) VISCALEX AT 77 [®] (polyacrylamide dispersion in mineral oil)	14
25	14) COLLAFIX PAP 404 [®] (polyacrylamide dispesion in mineral oil)	14
	TOTAL	1000

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Component A was prepared by slowly adding the cellulosic thickener to the benzyl alcohol/gamma-butyrolactone mixture with continued stirring.

Once cellulose dissolution had been completed, the aforesaid
5 components were added according to the numerical order indicated above until a homogeneous product was obtained.

Component B

Parts by wt.

35% hydrogen peroxide
10 (aqueous solution, 130 vol.) 1000

Process for the preparation and application of the final composition

The aforesaid formulations A and B, in a ratio equal to 100:40 by wt., were fed through separate suction pumps to an appropriate mixer where said components were mixed for approx. 5 sec.

15 The resulting composition was applied by spray gun to the substrate wherefrom the paint had to be removed.

EXAMPLE 2

Preparation of component A

		Parts by wt.
	1) benzyl alcohol	550
5	2) gamma-butyrolactone	250
	3) KLUCEL [®] (hydroxypropyl cellulose)	14
	4) ACTIROX 102 [®] (zinc phosphate and zinc molybdate)	47
10	5) HEUCOPHOS [®] ZPZ (zinc phosphate modified with an organic component)	9
	6) BUTROL [®] 23 (modified barium metaborate)	9
	7) zinc borate	9
15	8) CAB-O-SIL TS 720 [®] (water repellent amorphous silica)	13
	9) BUTYNE 497 [®] (1,4-bis(2-hydroxyethoxy)-2-butyne)	56
	10) REOX [®] (50% non-ionogenic polyurethane in 60/40 water-butyl glycol mixture)	42
	11) RED AW 305 [®] (water iron oxide)	1

Component B

25		Parts by wt.
	35% hydrogen peroxide (aqueous solution 130 vol.)	1000

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Process for the preparation and application of the final composition

The aforesaid formulations A and B, in a ratio equal to 100:40 by wt., were fed through separate suction pumps to an appropriate mixer where said components were mixed for approx. 5 sec.

- 5 The resulting composition was applied by spray gun to the substrate wherefrom the paint had to be removed.

EXAMPLE 3

Preparation of component A

		Parts by wt.
10	1) benzyl alcohol	550
	2) gamma-butyrolactone	250
	3) KLUCEL [®]	
	(hydroxypropyl cellulose)	14
	4) ACTIROX 102 [®]	
15	(zinc phosphate and zinc molybdate)	41
	5) BUTROL [®] 23	
	(modified barium metaborate)	41
	6) zinc borate	41
	7) CAB-O-SIL TS 720 [®]	
20	(water repellent amorphous silica)	13
	8) RHEOLATE [®] 420	
	(30% by wt. acrylic polymer aqueous emulsion)	42
	9) RED AW 305 [®]	
	(water iron oxide)	1

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Component B

Parts by wt.

35% hydrogen peroxide 1000
(aqueous solution 130 vol.)

5 Process for the preparation and application of the final composition

The aforesaid formulations A and B, in a ratio equal to 100:40 by wt., were fed through separate suction pumps to an appropriate mixer where said components were mixed for approx. 5 sec.

The resulting composition was applied by spray gun to the substrate
10 wherefrom the paint had to be removed.

EXAMPLE 4

Component A

Parts by wt.

	1) benzyl alcohol	545.171
15	2) gamma-butyrolactone	233.644
	3) KLUCEL® (hydroxypropyl cellulose)	13.200
	4) ACTIROX 102® (zinc phosphate and zinc molybdate)	119.048
20	5) BUTYNE® 497 (1,4 bis 2-hydroxy-ethoxy)-2-butyne	39.683
	6) REOX 2000® (50% non ionogenic polyurethane in 60/40 water-butyl glycol mixture)	30.000
25	7) CAB-O-SIL TS 720® (water repellent amorphous silica)	19.154

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8) RED AW 305^R

(water iron oxide)

0.100

Component B

Parts by wt.

5 35% hydrogen peroxide

1000

(aqueous solution 130 vol.)

Preparation of component A

Component A is prepared by slowly adding the cellulosic thickener to the mixture benzylalcohol-gammabutyrolactone maintained under stirring.

Once the dissolution of the cellulosic derivative is completed, the corrosion inhibitors are added to the mixture maintained under stirring. Once these compounds are uniformly dispersed, the remaining thickeners and the colouring agents are finally added, the mixture is maintained under stirring until obtaining a homogeneous composition.

Process for the preparation and application of the final composition

The aforesaid formulations A and B, in a ratio equal to 100:40 by wt., were fed through separate suction pumps to an appropriate mixer where said components were mixed for approx. 5 sec.

The resulting composition was applied by spray gun to the substrate wherefrom the paint had to be removed.

Paint removing test

With a view to checking the paint removing action of the product, some tests were conducted on panels of aluminium alloy 2024 T3, 0.5 mm thick, from AD AEROSPACE VoF, Sassenheim, painted according to one of the following four painting systems:

System 1 (cf. specification NT 10113)

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The panel was treated with a composition available under the trademark METAFLEX FCR[®] to clean and degrease the metallic surface before primer application.

5 The surface was then coated with a layer of isocyanate-catalysed epoxy polyurethane primer, available under the trademark AERODUR CF 37047^R and finally with an isocyanate-catalysed polyurethane finish available under the trademark AERODUR C21/100 UVR[®].

System 2 (cf. specification BMS 10-60)

10 The panel was treated with a composition available under the trademark ALODINE 1200[®] to clean and degrease the metallic surface before primer application.

The surface was then coated with a polyamide-catalysed epoxy primer denominated EPOXY PRIMER 37076 and finally with the same isocyanate-catalysed polyurethane finish as used in System 1.

15 **System 3**

The panel surface was anodized with chromic acid and coated first with an epoxy primer (EPOXY PRIMER 37057 NF), then with an isocyanate-catalysed polyurethane layer, available under the trademark AERODUR SEALER 42228[®], and finally with a finish based on the same
20 polyurethane as used in Systems 1 and 2.

System 4 (cf. specification BMS 10-72, type VI)

The metallic surface of the panel was treated with ALODINE 1200^R as used in System 2, coated with a polyamide-catalysed epoxy primer, denominated 10-P20-12, and finally with a isocyanate-catalysed
25 polyurethane finish, available under the trademark AVIOX[®].

Panels were 25 cm x 30 cm in size. Prior to product application, the panel had been divided into four sectors to avoid that superficial

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- imperfections (lower thickness of the film of paint, manufacturing defects, etc.), if any, might alter the results of the test. Each sector was coated with approx. 5 g of paint remover prepared as described in Example 1. The panel was positioned vertically to simulate the position of the aircraft surface. After treatment, the panels were maintained at ambient temperature and humidity until the film of paint was completely detached; they were then washed with a jet of water. The paint removing action was assessed vs. the percentage of paint removed.
- 10 The results obtained are shown in Table 1: the time of paint removal is expressed as a time interval, to include the time required for removing the paint from all four sectors.

Table 1

	Panel type	% Removal	Time
15	System 1	100	2-3 h
	System 2	100	4-6 h
	System 3	100	2-3 h
	System 4	100	1-1 h 20'

CLAIMS

1. Compositions capable of completely removing resinous coatings from essentially metallic substrates, containing hydrogen peroxide and gamma-butyrolactone and being characterized by the presence of benzyl alcohol at a concentration greater than or equal to that of gamma-butyrolactone, the concentration of said gamma-butyrolactone being lower than or equal to 20% by wt. of the total weight of said compositions.
2. Compositions capable of completely removing resinous coatings from essentially metallic substrates, containing:
- 5% to 30% by wt. hydrogen peroxide;
 - 20% to 50% by wt. water;
 - 5% to 20% by wt. gamma-butyrolactone;
 - 20% to 50% by wt. benzyl alcohol.
3. The compositions as claimed in claim 2 containing at least one of the following types of additives: corrosion inhibitors, thickeners, surfactants, and colouring agents.
4. The compositions as claimed in claim 3 containing at least one of the following types of thickeners: cellulosic derivatives, pyrogenic amorphous silica treated for water repellency, at least one polyacrylamide dispersion in mineral oil, aqueous dispersions of acrylic polymers or aqueous emulsions of non-ionic polyurethanes.
5. The compositions as claimed in claim 4, wherein the cellulosic derivatives are selected from the group consisting of hydroxypropyl cellulose, ethylcellulose, methylcellulose.
6. The compositions as claimed in claim 4, containing at the same time:
- 0.1% to 3% by wt., calculated on the total weight of said compositions, of hydroxypropyl cellulose having an average molecular weight ranging from 100,000 to 1,200,000;
 - 0.1% to 2% by wt., calculated on the total weight of said compositions, of amorphous silica made water repellent with silicone oil;



- 1% to 5% by wt., calculated on the total weight of said compositions, of one or more polyacrylamide dispersions in mineral oil.

7. The compositions as claimed in claim 4 containing at the same time:

5 - 0.1% to 3% by wt., calculated on the total weight of said compositions, of hydroxypropyl cellulose having an average molecular weight ranging from 100,000 to 1,200,000;

- 0.1% to 2% by wt., calculated on the total weight of said compositions, of amorphous silica made water repellent with silicone oil;

10 - aqueous dispersions of acrylic polymers or polyurethane aqueous emulsions, provided that the concentration of said aqueous dispersions or emulsions does not exceed 5%.

8. The compositions as claimed in claim 3 containing at least one of the following types of corrosion inhibitors: butynediol hydroxyethylethers,
15 gallic and metadigallic acid glycosidic esters, calcium silicate, sodium polyphosphate, thiourea in propargyl alcohol in 50% concentration, and metallic phosphates.

9. The compositions as claimed in claim 8 containing the following corrosion inhibitors: 1,4-bis(2-hydroxyethoxy)-2-butyne, sodium
20 polyphosphate, thiourea in propargyl alcohol, and calcium silicate, the total concentration of each corrosion inhibitor having to range from 2% to 10% by wt. of the total weight of said compositions.

10. The compositions as claimed in claim 8 containing the following corrosion inhibitors: zinc phosphate activated with zinc molybdate, zinc
25 phosphate modified with an organic component, or mixtures thereof, and optionally 1,4-bis(2-hydroxyethoxy)-2-butyne, the total concentration of said corrosion inhibitors in the final composition having not to exceed 15% by wt.

11. The compositions as claimed in claim 10 containing also metallic
30 borates in concentrations lower than or equal to 10% by wt.

12. The compositions as claimed in claim 3 containing at least one of the following types of surfactants: N-alkyl-pyrrolidone, in which the alkyl



group contains 8 to 18 carbon atoms, and sodium caprylamphohydroxypropylsulphonate.

13. The compositions as claimed in claim 12 containing the following surfactants: N-dodecyl-pyrrolidone and sodium caprylamphohydroxypropylsulphonate, the total concentration of said surfactants having to range from 1% to 5% of the total weight of said compositions.

14. The compositions as claimed in claim 3 wherein said colourant, present in a concentration of 0.01% to 0.1% by wt. of the total weight of said composition, is a pigment based on iron oxides.

15. A kit for producing compositions capable of completely removing resinous coatings from essentially metallic substrates, containing:

- a) from 5% to 30% by wt. hydrogen peroxide,
- b) from 20% to 50% by wt. water,
- c) from 5% to 20% by wt. gamma-butyrolactone,
- d) from 20% to 50% by wt. benzyl alcohol,

and, optionally, at least one of the following additives, i.e. corrosion inhibitors, thickeners, surfactants and colouring agents, said kit consisting of two separate components A and B, wherein component A contains benzyl alcohol, gamma-butyrolactone and optionally at least one of the additives mentioned above, and component B consists of a 35% aqueous solution of hydrogen peroxide, whereby, in use, component A and component B are mixed to produce said composition.

16. Process for the application of the composition as claimed in claim 15 to a painted substrate, said process consisting of the following steps:

- i) components A and B, in weight ratios ranging from 100:50 to 100:30, are fed through separate suction pumps to an appropriate mixer where mixing of said components takes place;
- ii) the resulting composition is applied by spray gun to the substrate wherefrom the paint is to be removed.

17. The process as claimed in claim 16, wherein said component A/component B ratio equals 100:40 by weight.



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