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(54) Cleaning composition and method of removing printing ink from surfaces.

(57) Compositions comprising two organic solvents which act synergistically, non-ionic and/or anionic surfactants and a relatively small proportion of cationic surfactant are disclosed for use in cleaning printing ink from surfaces. The solvents used together have considerably different kauri-butanol numbers.

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PATENTS ACT 1977

TITLE MODIFIED
see front page

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Application of Dawley Brook Papers Limited

Specification

Title: Cleaning composition and method.

Description of Invention:

THIS INVENTION relates to a composition suitable for use in cleaning and to a method of cleaning printing inks from apparatus and from personnel.

At present, undiluted organic solvents are used as cleaning fluids for removing printing inks from surfaces. The solvents are selected according to the character of the particular ink or inks to be removed. Solvents which are used include aromatic hydrocarbons, aliphatic alcohols, ketones and ethers, paraffins and halogenated hydrocarbons. Various disadvantages arise from the use of these solvents for the purpose mentioned. These disadvantages include the inflammability and toxicity of the solvents, particularly of their vapours, the volatility of the solvents, the effect of the solvents on the skin of persons using them, the insolubility of many of the solvents in water and the ability of the solvents to attack apparatus used in printing processes, for example to soften adhesive which secures a blanket on a roller. Solvents with high volatility generally have good ink-penetrating and dissolving ability but they evaporate rapidly and redeposit the dissolved ink. When the solvents come into contact with the skin, they tend to dry the skin and to cause dermatitis. Solvents which are readily soluble in water can be washed from the hands or from apparatus by means of water, but many of the solvents used have a character such that it is necessary,

once the ink has been dissolved in the solvent, to wash the solution away with further quantities of the solvent, either by rinsing the surface to be cleaned in the solvent or by wiping the surface with a cloth soaked in the solvent. These procedures are fairly expensive since there must be used considerably more solvent than is necessary merely to dissolve the ink which is to be removed. Furthermore, these procedures exaggerate the other disadvantages which have been mentioned herein.

It will be understood that not all solvents have all of the disadvantages hereinbefore mentioned and that different solvents suffer from these disadvantages to differing degrees. Nevertheless, the solvents which are used at the present time for removing printing inks are not entirely satisfactory and it is an object of the present invention to provide a cleaning composition which is more satisfactory than those now in use.

According to a first aspect of the invention, there is provided a cleaning composition comprising in admixture an organic solvent which is not completely miscible with water and a surfactant capable of forming an emulsion of the solvent in water.

A cleaning composition in accordance with the invention may also contain water and it is envisaged that in many circumstances a composition containing water will be used. The composition may be supplied as an aqueous composition or as a substantially non-aqueous composition. In either case, the composition may be diluted with water prior to use.

Water can be used to wash away from a surface to be cleaned a composition according to the invention which has been applied to the surface, together with any ink dissolved, emulsified or suspended in the composition. A composition according to the invention is less detrimental to the skin of a user than are the solvents used heretofore.

The composition preferably includes a second organic solvent. The second solvent is preferably at least partially miscible with water.

The first organic solvent may be immiscible with water and in compositions intended for cleaning dried inks from surfaces, the first solvent is immiscible with water.

The composition may be such that neither the first solvent nor the second solvent is completely miscible with water.

Preferably, the kauri-butanol number of one of the solvents exceeds the kauri-butanol number of the other of the solvents by at least twenty units. The difference between the kauri-butanol numbers may be at least 60 units

The kauri-butanol number of a solvent is an indication of the ability of that solvent to dissolve materials used in printing inks. The procedure for determining the kauri-butanol number of a solvent is described in standard test method 1133 published by the American Society for Testing and Materials.

The power of the composition as a solvent for printing inks can be determined by measuring the time required to remove a 25 mm square of the ink from a metal surface by rubbing the square of ink with a cloth impregnated with the composition and comparing this with the time required to remove a substantially identical ink square by means of a cloth impregnated with toluene. In order for consistent results to be achieved it is necessary for each square to be subjected to rubbing under substantially the same conditions but we have found that with a little practice a person can achieve consistent results rubbing the ink squares with the cloth by hand. It is also necessary for each ink square to have a similar character. For convenience, we have used ink squares which can be removed by rubbing with a cloth impregnated with toluene in 7 seconds.

The procedure we have used to determine the power of a composition as a solvent is as follows. Two 25 mm squares of printing ink are deposited on a clean steel plate. The ink is permitted to dry for a period such that rubbing for about 7 seconds with a cloth impregnated with toluene will be necessary to remove one of the squares. One of the squares is then rubbed with a cloth impregnated with toluene and the time required to remove the square, T(tol) is noted. The other square is rubbed with a cloth impregnated with the composition and the time required to remove the square T(comp) is noted. The time which would be required for removing the ink square by means of the composition if the ink square could be removed in 7 seconds by toluene is calculated from the following expression:-

$$\text{corrected time } (t) = T(\text{comp}). \frac{7}{T(\text{tol})}$$

all time being in seconds.

We have found that if the corrected time required for undiluted solvents having known kauri-butanol numbers is used to plot a graph of $\log_e$ of the kauri-butanol number against time in seconds, there is produced a straight line according to the equation :-

$$\log_e N = 4.92 - 0.038\ t$$

where N is the kauri-butanol number and t is the time in seconds required for removal of a 25 mm square of printing ink from a surface by rubbing with a cloth impregnated with the solvent and which square can just be removed in 7 seconds by rubbing with a cloth impregnated with toluene.

To calculate the power P of a composition as a solvent for printing ink we use the expression :-

$$\log_e P = 4.92 - 0.038\ t$$

where t is the time in seconds required for removal of a 25 mm square of printing ink from a surface by rubbing with a cloth impregnated with the composition and which square can just be removed in 7 seconds by rubbing with a cloth impregnated with toluene.

We have found that the power of examples of compositions in accordance with the invention having two organic solvents exceeds the weighted average of the respective powers of composition each comprising a single solvent and which could be mixed to form the composition comprising two solvents. By weighted average of the powers we mean :-

$$\frac{P_1 \cdot R + P_2}{R + 1}$$

where P_1 is the power of the first single solvent composition

P_2 is the power of the second single solvent composition and

R is the ratio

$$\frac{\text{weight of first single solvent composition}}{\text{weight of second single solvent composition}}$$

The proportion by weight of the solvent with the lower kauri-butanol number preferably exceeds the proportion by weight of the solvent with the higher kauri-butanol number. The ratio of the respective proportions of solvents may be in the range 2:1 to 5:1.

The first solvent may be selected from the group comprising halogenated, especially chlorinated, hydrocarbons and ketones. The second solvent may be selected from the group comprising ethers and aromatic hydrocarbons. The preferred ethers are those containing hydroxyl groups, particularly mono-ethers of glycols.

Alternatively, the first solvent may be selected from the group comprising ethers and aromatic hydrocarbons, the second solvent being a mixture of aliphatic hydrocarbons.

There is also provided according to the invention a method of removing printing ink from a surface wherein there is applied to the surface a composition according to the first aspect which is subsequently removed by rinsing with water or wiping with a medium impregnated with water.

The constitution of a number of examples of compositions in accordance with the invention is given in Table I and various parameters of each of these compositions are given in Table II. For convenience, the organic solvents of the compositions identified in Table I are designated by the letters S to Z as follows:-

S	odourless kerosine	- immiscible with water
T	naptha	- immiscible with water
U	4-methoxy-4-methyl-2-pentanone	- partly miscible with water
V	2-ethoxy ethanol	- partly miscible with water
W	mixture of aromatic hydrocarbons with a boiling point of 165°C	- immiscible with water
X	methylethylketone	- partly miscible with water
Y	dichloromethane	- immiscible with water
Z	1,1,1-trichloro-ethane	- immiscible with water

In Table I, anionic surfactants are designated by the letter A and a mixture of non-ionic and anionic surfactant is designated by the letter M. Proportions of cationic surfactant present in the compositions are shown separately. The letter N is used in Table I to represent non-ionic surfactant.

TABLE I

Composition No.	First Solvent	Second Solvent	Third Solvent	First Surfactant	Cationic Surfactant	Water	Plasticiser
1.	Y 35.1%	-	-	M 17.5%	3.5%	43.9%	-
2.	W 34.5%	-	-	M 19%	3.4%	43.1%	-
3.	W 25.9%	Y 8.6%		M 19%	3.4%	43.1%	-
4.	Z 36.4%	-	-	M 16.4%	1.8%	45.4%	-
5.	W 34.5%	-	-	M 19%	3.5%	43%	-
6.	Z 9.1%	W 27.3%	-	M 16.4%	1.8%	45.4%	-
7.	S 47.6%	-	-	M 17.9%	4.8%	29.7%	-
8.	Y 35.1%	-	-	M 17.5%	3.5%	43.9%	-
9.	S 27.5	Y 9.2%	-	M 13.8%	3.7%	45.8%	-
10.	Y 36.1%	-	-	M 18.1%	0.7%	45.1%	-

Composition No.	First Solvent	Second Solvent	Third Solvent	First Surfactant	Cationic Surfactant	Water	Plasticiser
11.	W 35.4%	-	-	M 19.5%	0.9%	44.2%	-
12.	W 28.3%	Y 9.4%	-	M 14.2%	0.9%	47.2%	-
13.	S 47.1%	-	-	M 18.8%	4.7%	29.4%	-
14.	Y 35.1%	-	-	M 17.5%	3.5%	43.9%	-
15.	S 26.8%	-	Y 8.9%	M 16.07%	3.6%	44.6%	-
16.	W 32%	X 5.6%	-	M 17.2%	1.4%	42.6%	1.2%
17.	Z 22.1	S 14.7%	X 1.5%	N 24.1%	0.7%	36.8%	-
18.	Z 22.1%	S 14.7%	U 1.5%	N 24.1%	0.7%	36.8%	-
19.	W 16.6%	Y 5.5%	-	N 34.1%	-	43.8%	-
20.	X 28.4%	W 28.4%	-	M 28.4%	-	14.2%	0.6%

Composition No.	First Solvent	Second Solvent	Third Solvent	First Surfactant	Cationic Surfactant	Water	Plasticiser
21.	X 33.3%	W 33.3%	-	M 33.4%	-	-	-
22.	W 16.4%	Y 5.5%	-	M 11.8%	0.2%	65.3%	0.7%
23.	Z 23.4%	S 15.6%	U 1.6%	M 19.5%	0.8%	39.1%	-

TABLE II

Composition No.	kauri-butonal numbers of undiluted solvents			Solvent Power	Weighted Average Power	Ratio of weights of Solvents	Ratio of weights of surfactants
	First	Second	Difference				
1.	136	-	-	71.5	-	-	5:1
2.	90	-	-	94.6	-	-	5.5:1
3.	136	90	46	100.5	88.9	1:3	5.5:1
4.	124	-	-	92.8	-	-	9:1
5.	90	-	-	94.6	-	-	5.5:1
6.	124	90	34	97.5	94	1:3	9.1:1
7.	30	-	-	below 20	-	-	3.8:1
8.	136	-	-	71.5	-	-	5:1
9.	30	136	106	73	below 36	3:1	20:1
10.	136	-	-	below 20	-	-	26:1
11.	90	-	-	87.4	-	-	22:1

Composition No.	kauri-butonal numbers of undiluted solvents			Solvent Power	Weighted Average Power	Ratio of weights of Solvents	Ratio of weights of surfactants
	First	Second	Difference				
12.	90	136	46	90	below 70	3:1	15:1
13.	30	-	-	below 20	-	-	4:1
14.	136	-	-	71.5	-	-	5:1
15.	30	136	106	66	-	3.2:1	4.5:1
16.	90	130	40	108.8	-	5.7:1	12.1:1
17.	124	30	Third 130 -	88	-	15:10:1	32.6:1
18.	124	30	- -	84	-	15:10:1	32.6:1
19.	90	136	46	86	-	3:1	-
20.	130	90	40	119	-	1:1	-
21.	130	90	40	122.7	-	1:1	-
22.	90	136	46	53.5	-	3:1	51.5:1
23.	124	30	- -	87	-	15:10:1	25:1

TABLE III

Example	Organic Solvent	Water	First non-ionic surfactant	Second non-ionic surfactant	Mixture of anionic and non-ionic surfactant	Cationic Surfactant	Total Surfactant
1	23.6	39.4	31.5	5.5	0	0	37
2	22.5	37.6	30.1	9.8	0	0	39.9
3.	25	41.5	32	0	0	1.5	33.5
4.	28.6	47.6	0	0	23.8	0.	23.8
5.	29.8	49.7	0	0	19.8	0.7	20.5

Compositions 1 and 2 of Table II each comprise a single, different solvent. The other constituents of compositions 1 and 2 are the same and are present in substantially the same proportions. Composition 3 comprises two organic solvents andcan be formed by mixing appropriate quantities of compositions 1 and 2. Except for the organic solvents, the constituents of compositions 2 and 3 are present in the same proportions. It will be noted that the total proportion of organic solvent in composition 3 is the same as the proportion of organic solvent in composition 2 and that the solvent power of composition 1 is less than that of composition 2. The solvent power of composition 3 exceeds the respective solvent powers of compositions 1 and 2. This demonstrates the synergistic action of the two solvents. The synergistic effect of different combinations of solvents can be shown by a comparison of compositions 4 and 5 with composition 6, of compositions 7 and 8 with composition 9 and of compositions 10 and 11 with composition 12.

Compositions comprising two solvents, especially solvents having respective kauri-butanol numbers which differ considerably, can achieve a required solvent power at lower cost than the same solvent power can be achieved by a composition comprising a single solvent and provide the further advantages of relatively reduced inflammability and volatility and a less harmful effect on the hands of users than is the case with compositions comprising a single solvent and having the same solvent power.

All of the preferred compositions comprise a second surfactant which is cationic. The first of the surfactants may be anionic but is preferably non-ionic. In a case where the composition comprises three surfactants these are preferably non-ionic, cationic and anionic

respectively. The proportion of the cationic surfactant may be less than the respective proportions of the non-ionic and anionic surfactants. In a case where the composition comprises a non-ionic surfactant and a cationic surfactant but no anionic surfactant, the weight of non-ionic surfactant preferably exceeds the weight of the cationic surfactant. The ratio of the respective proportions of the surfactants may be within the range 15:1 to 30:1.

The presence of a relatively small proportion of a cationic surfactant enables a substantial reduction in the proportion of non-ionic and/or anionic surfactant, as compared with the proportion necessary in the absence of any cationic surfactant. This is illustrated by the examples of compositions listed in Table III. Each of these compositions has a power of approximately 89 and comprises the same organic solvent, a mixture of aromatic hydrocarbons, this mixture being the sole organic solvent in the compositions of Table III.

In Table III, the proportions of the constituents in each example are indicated by weight. From a comparison of examples 1, 2 and 3, it can be seen that the addition of a relatively small proportion of cationic surfactant enables relatively larger reductions to be made in the proportions of the non-ionic surfactants. Examples 4 and 5 show that where a mixture of anionic and non-ionic surfactant is used, the total mount of surfactant necessary to provide a stable composition having a power of approximately 89 can be reduced by the inclusion of a relatively small proportion of cationic surfactant. Furthermore, the composition according to example 4 is not stable at temperatures

below 20°C. Below this temperature, the composition separates into aqueous and non-aqueous phases; whereas a composition according to example 5 is stable at temperatures below 20°C. Each of the examples listed in Table III contains just sufficient surfactant to provide a stable emulsion when diluted by any selected amount of water.

Each of the compositions listed in Table I contains water in a proportion such that the composition is suitable for dissolving or dispersing printing ink. The water could be omitted when the composition is prepared for sale and added to dilute the composition for use.

With the exception of compositions 1, 7, 8, 10, 13 and 14, each of the compositions listed in Table I can be further diluted with any selected volume of water without breakdown of the emulsion occurring. Once printing ink has been dissolved in a quantity of the composition having the proportions set out in Table I, the dissolved ink can be washed away with water. It will be noted that the compositions which cannot be diluted with any selected volume of water without breakdown of the emulsion occurring are compositions comprising a single organic solvent. All of the compositions which contain more than one organic solvent can be diluted to any degree with water.

The compositions can be applied to a surface from which printing ink and/or other matter is to be removed by spraying, brushing or wiping the composition onto the surface. The composition, together with dissolved ink or other matter, can then be removed by wiping or by

rinsing with water. Wiping on of the composition is, of course effected by means of a cloth or other absorbent medium impregnated with the composition. Wiping off of the composition containing dissolved ink may be effected either by means of a cloth or other absorbent medium impregnated with the composition or by means of an aborbent medium impregnated with water. In either case, the printing ink or other matter to be removed from the surface will tend to migrate into the absorbent medium so that the surface of the absorbent medium will not become soiled to the same degree as would occur if all of the matter wiped from the surface remains on the surface of the absorbent medium.

In a case where a mixture of anionic, cationic and non-ionic surfactants is used, the proportion by weight of cationic surfactant is preferably less than the respective proportion by weight of the anionic and non-ionic surfactants. The cationic surfactant may be a tertiary amine having two polyoxyethylene groups and a C12 to C18 alkyl group attached to the nitrogen atom.

The plasticiser used in certain of the compositions of Table I is a plasticiser, the use of which is known in coating compositions and which is the ester of an aliphatic carboxylic acid. 2,2,4- trimethyl 1,3-pentandiol diiobutyrate is a suitable plasticiser.

Claims:-

1. A cleaning composition comprising in admixture an organic solvent which is not completely miscible with water and a surfactant capable of forming an emulsion of the solvent in water.

2. A composition according to claim 1 wherein the solvent is immiscible with water.

3. A composition according to claim 1 or claim 2 further comprising a second organic solvent, the second solvent being at least partly miscible with water.

4. A composition according to any preceding claim wherein the kauri-butanol number of one of the solvents exceeds the kauri-butanol number of the other of the solvents by at least 20.

5. A composition according to claim 1 further comprising a second organic solvent and having a solvent power exceeding the weighted average of the respective solvent powers of two sub-compositions which differ from each other only in respect of the organic solvent content, which can be mixed to form the composition comprising two organic solvents, one of which sub-compositions comprises the first organic solvent but not the second organic solvent and the other of which sub-compositions comprises the second organic solvent but not the first organic solvent.

6. A composition according to claim 4 wherein the proportion by weight of the solvent with the lower kauri-butanol number exceeds the proportion by weight of the solvent with the higher kauri-butanol number.

7. A composition according to any preceding claim further comprising a second surfactant which is cationic, the first surfactant being anionic and/or non-ionic.

8. A composition according to claim 7 wherein the proportion by weight of the first surfactant exceeds the proportion by weight of the second surfactant.

9. A method of removing printing ink from a surface wherein there is applied to the surface a composition according to any one of claims 1 to 8 and the composition is subsequently removed from the surface by rinsing the surface with water or wiping the surface with an absorbent medium impregnated with water.

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EUROPEAN SEARCH REPORT

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Application number

EP 79 300 219.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - A - 2 628 480 (L'OREAL) *claims 1 and 2* --	1,2
A	DE - B - 1 068 839 (M.J.B. LADEUZE et al) *complete document* --	
A	DE - C - 1 144 427 (O. BAUMBACH) *complete document* ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 11 D 3/43
C 11 D 3/44

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 09 D 11/02
C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	02.05.1979	SCHULTZE

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