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GB 1581333 A **EP 0309173 A**

(58) Field of Search:
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Other: **ONLINE: WPI, EPODOC, TXTE**

(54) Abstract Title: **Volatile compositions having an end-of-life indication**

(57) A non-aqueous composition comprising a halochromic dye, a fragrance material, a non-volatile base or acid, and a highly polar, low volatile solvent is disclosed. The composition changes its colour when the predominant part of the fragrance material has evaporated over time. The preferred composition comprises Bromocresol Green as the dye, triethanolamine as the non-volatile base, dipropylenglycole as the solvent, and a fragrance composition. Also claimed is an air-freshener device in which a composition of the present invention is absorbed or adsorbed in a material selected from paper, textiles, felt-type materials, wovens and non-wovens, glass fibre filters and crystals.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

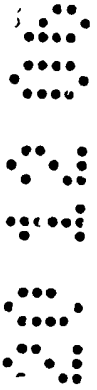
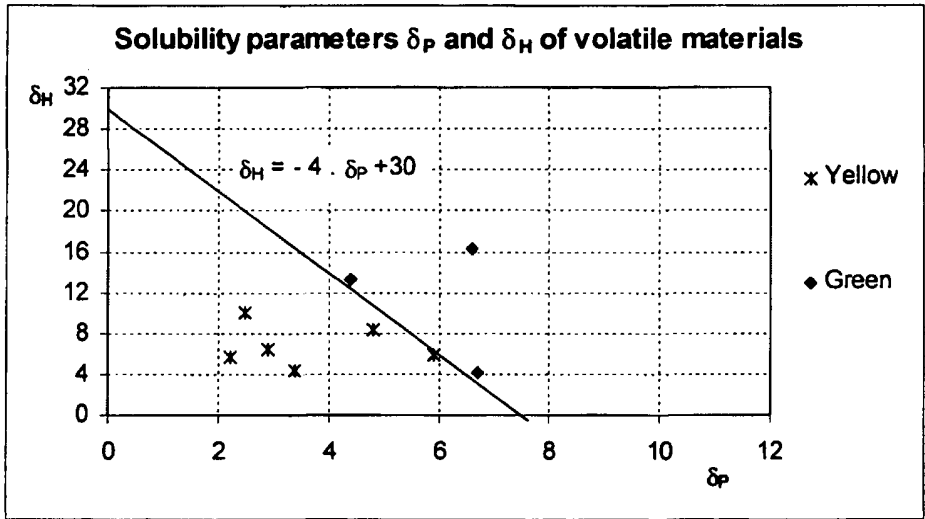
This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1995

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Fig. 1



ORGANIC COMPOSITION

The present invention is generally directed to volatile compositions having an end-of-life indication and to systems comprising them. Particularly the present invention is generally directed to air-freshener systems useful in dispensing volatile substances, e.g. fragrance materials, which also include an end-of-life indicator.

Air-freshener systems typically include a volatile material, often included within a carrier substance which, when exposed to the air-space of the ambient environment, volatilizes over time, until essentially all of the volatile material has been delivered from the air-freshener system. While such a system is elegant in its simplicity and is effective, it suffers from the shortcoming that typically there is no visibly discernable indicator of the end of the useful life of the air-freshener system provided to the user of the device. There is thus nothing to indicate that a further air-freshener system should be purchased and used in the place of the depleted system, or that the depleted system should be refilled with a fresh supply of volatile material.

To overcome this shortcoming, the prior art has proposed various solutions. Indicator systems specially intended for air freshener systems are, for example, described in US Patent 4,128,508, which indicator system is based on the change in color of a pH indicator combined with a slowly evaporating acid or base. Such systems have the disadvantage that the choice of suitable volatile acids and bases is limited, inter alia, because they often have a strong and usually undesirable smell of their own. In addition, this system only works for aqueous-based perfume compositions.

International Patent application WO 03/031966 describes a system, which is based on volatile dyes, which are coated on a substrate thereby coloring the substrate. As the volatile dye evaporates over time, the substrate changes color. While such a system provides certain advantages, nonetheless it requires that a substrate be coated in a first step before the fragrance is added.

While the prior art provides certain useful systems, nonetheless there remains a real and continuing need in the art to provide further means which provide an indication of the consumption of a volatile, in particular a fragrance.

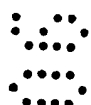
Surprisingly it has been found that halochromic dyes, i.e. materials which are known to the person skilled in the art as materials that change their color when pH changes occur, when used with non-aqueous composition, change their color as the volatile material evaporates over time, thus indicating that the composition has become ineffective.

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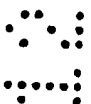
Accordingly, the present invention refers in one of its aspects to a non-aqueous composition comprising a halochromic dye, a fragrance material, a non-volatile base or acid, and a highly polar, low volatile solvent, said composition changing its color when the predominant part of the fragrance material has evaporated over time.

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By "non-aqueous composition" is meant a composition, in particular a liquid, which is essentially free of water, i.e. containing less than 1% by weight of water based on the total composition.

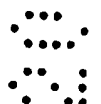


15 Suitable fragrance materials may be selected from the extensive range of natural products and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles. Such fragrance materials are described, for example, in S. Arctander Perfume Flavors and Chemicals Vols. 1 and 2, Arctander, Montclair, NJ USA 1989.



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By "non-volatile" is meant any material having a maximum vapor pressure of 0.025mm Hg (preferably a maximum of 0.01mm Hg) at 20°C. Non-volatile bases may be selected from the non-limiting list consisting of triethanolamine (TEA), 4-methylphenyl amine and 4-dimethylaminopyridine (DMAP). Non-volatile acids may be selected from the non-limiting list



25 consisting of citric acid, lauric acid, stearic acid, linoleic acid, acrylic acid, pyruvic acid, nicotinic acid, acetylsalicylic acid, and the like.

Examples of highly polar, low volatile solvents include dipropylenglycole (DPG), triethyleneglycol (TEG), propyleneglycol (PG), glycerine, 2-methyl-1,3-propanediol,
30 tripropyleneglycol methyl ether (Dowanol TPM), and the like.

Preferably, the highly polar, low volatile solvent has a maximum vapor pressure of 0.1mm Hg at 20°C. By "highly polar" is meant that the selected solvent is able to solubilize more or

at least 0.1 weight % of the halochromic dye which is intended to be used in the composition..

The composition according to the present invention preferably comprises at least 40 weight % , e.g. 80 weight % or more, preferably 90 weight % or more, such as 95%, of a fragrance material based on the total composition.

By "halochromic dye" is meant any material known to be a material that changes color when pH changes occur. Suitable halochromic dyes may be selected from the non-limiting list consisting of 2,4-Dinitrophenol (CAS 51-28-5), Alizarin sodium sulfonate (CAS 130-22-3), Alizarin yellow (CAS 476-66-4), α -Naphtholbenzein (CAS 145-50-6), α -Naphtholphthalein (CAS 596-01-0), α -Naphthyl red (CAS 1260-17-9), Azolitmin (CAS 1395-18-2), Oracet blue 2R (CAS 4395-65-7), Bromocresol green (CAS 76-60-8), Bromocresol purple (CAS 115-40-2), Bromophenol blue (CAS 115-39-9), Bromothymol blue (CAS 76-59-5), Clorophenol red (CAS 4430-20-0), Congo red (CAS 117-92-0), Cresol red (CAS 1733-12-6), Crystal violet (CAS 548-62-9), Diazo violet (CAS 6528-37-6), Methyl yellow (CAS 60-11-7), Methyl orange (CAS 547-58-0), Methyl red (CAS 493-52-7), Methyl violet 2B (CAS 8004-87-3), Neutral red (CAS 553-24-2), Nile blue (CAS 3625-57-8), p-Ethoxychrysoidine (CAS 94-10-0), p-Nitrophenol (CAS 100-02-7), Pentamethoxy red (CAS 1755-51-7), Phenol red (CAS 143-74-8), Phenolphthalein (CAS 77-09-8), Poirrier's blue (CAS 1400-96-0), Rosolic acid (CAS 603-45-2), Salicyl yellow (CAS 584-42-9), Tetrabromphenol blue (CAS 4430-25-5), Thymol blue (CAS 76-61-9), Thymolphthalein (CAS 125-20-2) and Trinitrobenzoic acid (CAS 129-66-8)

In a preferred embodiment, the halochromic dye is selected from the triphenylmethane family of so-called triarylmethane dyes, for example, Bromocresol green.

Extensive research revealed that halochromic dyes used in compositions according to the present invention change their color as a consequence of to the Hansen polar solubility parameter (δ_p) and the Hansen hydrogen bonding solubility parameter (δ_H) of the fragrance material in which the dye is dissolved. These parameters may be evaluated as disclosed, for example, in "Hansen Solubility Parameters: A User's Handbook" (Charles M. Hansen, CRC Press, 2000) or/and by using software available on the market, such as Molecular Modeling Pro from www.Chemistry-Software.com. The data given in Table 1 below have been calculated using the algorithm of Molecular Modeling Pro from Chemistry ChemSW for

calculating δ_p and δ_H based on group contribution as described on page 9-10 of "Hansen Solubility Parameters: A User's Handbook" (Charles M. Hansen, CRC Press, 2000).

Fig. 1 illustrates, graphically, the data presented in Table 1, and more specifically the relation between the solubility parameters δ_H and δ_p .

As is further illustrated by the examples, Bromocresol green provides a clearly visible color change indicator from yellow to blue as the fragrance material evaporates over time, and is thus preferred. It has been found that non-aqueous compositions comprising

- 10 - Bromocresol green
- fragrance materials having a polar solubility parameter (δ_p) $\leq 7.5(\text{MPa})^{1/2}$, a hydrogen bonding solubility parameter (δ_H) $\leq 30 (\text{MPa})^{1/2}$ and $\delta_H \leq -4 * \delta_p + 30$,
 - high polar, low volatile solvent, and
 - a non-volatile base, such as triethanolamine,
- 15 change their color from yellow to blue when the predominant part of the fragrance material has evaporated over time thus indicating that the composition has become ineffective.

By "predominant part" is meant that more than 50 weight % of the fragrance material, preferably at least 75%, e.g. at least 80%, is evaporated.

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Accordingly, the present invention refers in a further aspect to a non-aqueous composition comprising

- a) Bromocresol green,
- b) a fragrance composition consisting of at least 30 weight %, preferably at least 50 weight %, e.g. 60, 70 or 80 weight %, of a fragrance material having a polar solubility parameter (δ_p) $\leq 7.5(\text{MPa})^{1/2}$, a hydrogen bonding solubility parameter (δ_H) $\leq 30 (\text{MPa})^{1/2}$ and $\delta_H \leq -4 * \delta_p + 30$;
- c) high polar, low volatile solvent; and
- d) a non-volatile base.

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The composition according to the present invention may further comprise excipients generally used in combination with air-freshener compositions, such as malodorant counteracting compounds, antibacterials and insect repellents.

The composition provided by this invention can be absorbed into absorbent bases such as paper, textiles, felt-type materials, wovens and nonwovens, bonded or sintered synthetic or natural polymer powders, cellulose or unglazed ceramics, or adsorbed onto glass fiber filters, or crystals such as rock salt crystals or silica gel crystals.

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The invention is now further described with reference to the following non-limiting examples. These examples are for the purpose of illustration only and it is understood that variations and modifications can be made by one skilled in the art.

10 Example 1: non-aqueous compositions comprising Bromocresol green

95 g of a volatile material as indicated in the table below were mixed with 5 g of a blend of Bromocresol green, triethanolamine (TEA) and dipropylene glycol (DPG) (0.7 weight % TEA, 0.1 weight % Bromocresol green and 99.2 weight % DPG), resulting in a yellow or green

15 compositions. Each individual mixture changed its color to blue after approximately 90 weight % of the volatile material was evaporated over time.

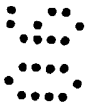
Table 1: solubility parameters δ_P and δ_H of volatile materials

volatile material	δ_P	δ_H	color of the mixture
acetophenone	6.7	4.2	green
isopropyl alcohol	6.6	16.2	green
phenyl ethyl alcohol	4.4	13.2	green
aldehyde c12 mna (2-methylundecanal)	3.4	4.4	yellow
capronaldehyde	5.9	5.8	yellow
citronellyl acetate	2.2	5.6	yellow
ethyl acetate	4.8	8.3	yellow
cis-3- hexen-1-ol	2.9	6.4	yellow
undecavertol (4-methyl-3-decen-5-ol)	2.5	10.0	yellow

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Mapping the two solubility parameters δ_P and δ_H the curve ($\delta_H = -4 \delta_P + 30$) shows a clear defined boundary between volatile compounds showing a yellow coloration when mixed with

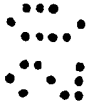
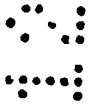
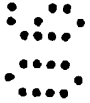
a mixture comprising Bromocresol green, DPG and TEA and a green coloration respectively (see Figure 1).



Claims

1. A non-aqueous composition comprising a halochromic dye, a fragrance material, a non-volatile acid or base, and a highly polar, low volatile solvent, said composition changing its color when the predominant part of the fragrance material has evaporated over time.
2. A composition according to claim 1 wherein the highly polar, low volatile solvent has a maximum vapour pressure of 0.1mm Hg at 20°C.
3. A composition according to claim 1 or claim 2, wherein the non-volatile acid or base has a maximum vapour pressure of 0.01mm Hg at 20°C.
4. A composition according to any one of the preceding claims wherein the highly polar low volatile solvent is selected from the list consisting of dipropylenglycole , triethyleneglycol, propyleneglycol, glycerine, 2-methyl-1,3-propanediol and tripropyleneglycol methyl ether.
5. A composition according to any one of the preceding claims wherein the non-volatile acid is selected from the group consisting of citric acid, lauric acid, stearic acid, linoleic acid, acrylic acid, pyruvic acid, nicotinic acid and acetylsalicylic acid.
6. A composition according to any one of claims 1-4 wherein the non-volatile base is selected from the group consisting of triethanolamine, 4-methylphenyl amine and 4-dimethylaminopyridine.
7. A composition according to claim 1 wherein the halochromic dye is Bromocresol green and the non-volatile base is triethanolamine.
8. A composition according to claim 7 comprising
 - a) Bromocresol green,
 - b) a fragrance composition consisting of at least 30 weigh % of a fragrance material having a polar solubility parameter (δ_p) $\leq 7.5(\text{MPa})^{1/2}$, a hydrogen bonding solubility parameter (δ_H) $\leq 30 (\text{MPa})^{1/2}$ and $\delta_H \leq -4 * \delta_p + 30$;
 - c) triethanolamine; and
 - d) dipropylenglycole.

9. An air-freshener device comprising a composition as defined in any one of the preceding claims.
10. An air-freshener device according to claim 9 further comprising a means to which the composition is absorbed or adsorbed.
11. A device according to claim 10 wherein the absorbent is selected from paper, textiles, felt-type materials, wovens and nonwovens.
12. A device according to claim 10 wherein the adsorbent is selected from glass fiber filters and crystals.



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Application No: GB0624857.9

Examiner: Mr Chris Archer

Claims searched: 1-12

Date of search: 11 April 2007

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-3, 5, 9-12	EP 0309173 A (S.C. JOHNSON) see whole document, especially page 3 lines 31 to 48, examples 3 and 22-29.
A	-	GB 1581333 A (UNILEVER) see whole document, especially the examples.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X:

Worldwide search of patent documents classified in the following areas of the IPC

A61K; A61L; A61Q; G01N

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, TXTE

International Classification:

Sub Class	Sub Group	Valid From
A61L	0009/01	01/01/2006
A61L	0009/04	01/01/2006
A61Q	0013/00	01/01/2006