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(54) A PROCESS, APPARATUS AND COMPOSITION
FOR PREVENTING THE FORMATION OF A
SKIN ON THE SURFACE OF PAINTS AND
RELATED MATERIALS

(71) We, HENRY BURROWS DISON and GORDON FRANK DISON of 16 Crescent Drive, Helsby, Cheshire; and "Crae", Royleen Drive, Frodsham, Near Warrington; respectively; both British subjects, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process, apparatus and composition for preventing the formation of a skin on the surface of paints and related materials, such as varnishes, coatings, sealers and putty, which dry by an oxidation/polymerisation mechanism.

A problem which as heretofore been experienced with paints and the above related materials is that after the initial use of a paint contained within a container, it is often noted, upon a subsequent use of the paint, that a skin has formed on the surface thereof.

The formation of a skin on the surface of a paint contained within a container causes certain disadvantages to the user. In particular, removal of the skin is both messey and time consuming. Further, certain thin skins which are formed on the surface of the paint are virtually impossible to remove other than by utilisation of a sieve. Also, unremoved bits of the skin which tend to be left in the paint cause a spoiling of the paint finish and both time and trouble are involved in removal thereof from a painted surface.

Moreover, it also has to be borne in mind that the removal of successive skins from the surface of the paint can alter the original formulation of such paint as the lighter elements contained in such paint tend to rise to the surface and are therefore removed disproportionately when the skin is

removed. A paint, for example, could therefore suffer reduction in gloss and alteration in colour.

A further disadvantage is that removal of a skin is obviously a waste of expensive paint. It is probable that 10% to 20% of the original volume of paint within a container is discarded in skin removal and as skinned or hardened residue. Moreover, skin formation around the region of the container in which its cover is applied can cause difficulties in removing the cover and upon subsequent action can cause deformation of the cover which in turn provides a poor seal resulting in even greater skin formation on the surface of the paint.

It is common experience that paint in partly used containers is more prone to skinning than paint in new unopened containers. Whilst paint when originally supplied occupies nearly all the enclosed volume within the container, following subsequent use or usages, more oxygen will be enclosed within the container thus increasing the likelihood of polymerisation of the paint and the formation of a skin on the surface thereof.

Although paint is usually formulated with an antioxidant to prevent skin formation prior to the initial use of the paint and to provide some protection during its early use, it is not feasible for sufficient antioxidant to be incorporated in manufacture to give protection throughout the life of a tin of paint which has been in use on several occasions and in which the ullage has been substantially increased. We have found that even new paint will readily skin if sealed within a container in which the ullage is sufficiently large.

It is an object of the present invention to at least minimize and preferably prevent the formation of a skin on the surface of a paint contained in a container subsequent to its

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initial use and irrespective of the amount of paint within the container.

We have surprisingly discovered that regardless of the amount of oxygen present in the container and regardless of the number of occasions the paint has been in use, the formation of a skin on the surface of a paint or related material which dries by a process of oxidation/polymerisation contained within a container can be substantially reduced and in most cases prevented by supplying and maintaining in the air space above the paint or related material a sufficient concentration of vapour of a suitable antioxidant, which is effective in its vapour phase.

According to the present invention there is provided a process for the prevention, or at least substantial prevention, of the formation of a skin upon the surface of a paint or related material which dries by a process of oxidation/polymerisation within a container, subsequent to its initial use and irrespective of the amount of paint or related material within the container, comprising supplying and maintaining in the air space above the paint or related material a sufficient concentration of vapour of an antioxidant which is effective in its vapour phase.

Furthermore, this vapour may be readily supplied and maintained by utilizing a suitable vaporisable liquid antioxidant which is effective in its vapour phase.

We have also discovered that the antioxidant vapour may be conveniently supplied and maintained by soaking a suitable pad or like device with a vaporisable liquid antioxidant, or a composition containing such antioxidant, and suspending the pad in the air space above the paint or related material. The pad may be of felt, absorbent paper, foamed plastics material or other suitable material and may for instance be suspended below the lid of the container by means of a suitable suspension means, such as a magnet, to which the pad is attached.

The liquid antioxidant or composition containing such antioxidant may alternatively be located in one or more dishes or housings separate from the paint or related material, allowing vaporisation to take place directly from the liquid surface or from wicks or pads connected thereto.

Furthermore we have discovered that prior to replacing the lid of the container following each usage of the paint or related material a small amount of liquid antioxidant, or a composition containing such antioxidant, can be deposited directly onto the surface or a portion of the surface of the paint or related material and left thereon without mixing, thus allowing it to substantially vaporise into the air space

above the paint or related material. This method allows small amounts of the antioxidant to be effective, irrespective of the level of paint or related material within the container, without utilizing additional apparatus and without unduly altering the composition of the paint or related material.

It is also possible to acquire sufficient concentration of antioxidant at the paint/air interface by stirring into the paint substantially larger quantities of liquid antioxidant than would otherwise be required if deposited onto the surface and allowed to remain thereon. This method however is likely to result in the paint becoming overloaded with antioxidant which may adversely affect properties of the paint such as viscosity, drying time and film hardness.

An aspect of the invention is the provision of a device such as a suitable pad upon which the antioxidant, or a composition containing such antioxidant, preferably in liquid form, can be located above the surface of the paint within a container. The pad will be of suitable size to hold sufficient liquid antioxidant and provide sufficient surface area to allow adequate vaporisation of the antioxidant to take place. The pad may be of felt or other suitable absorbent material and may for instance be attached to the lid of the container by means of a magnet. There are obviously other ways of suspending the pad such as for instance by means of a suction cup or a suitable adhesive or by means of a support from the base or sides of the container or by means of a fitting integral with the lid of the container. Also, if a large container is involved, then a plurality of such pads may be used. The liquid antioxidant or a composition containing the antioxidant could be supplied to the user for instance in a bottle suitable for charging and recharging the pad as required, or alternatively pads could be supplied already charged with antioxidant.

Another aspect of the invention is that liquid antioxidant, or a composition containing such antioxidant, may be located in a device such as a dish or housing separate from the paint, allowing vaporisation to take place directly from the surface of the antioxidant or from a wick or pad connected thereto.

A further aspect of the invention is the method whereby the liquid antioxidant, or a composition containing such antioxidant, may be deposited onto the surface or onto a portion of the surface of the paint and allowed to remain substantially thereon without stirring or mixing, thus allowing the antioxidant to substantially vaporise into the air space above the paint. This method of treatment would preferably be performed at

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the end of each period in which the paint had been in use, and necessary instructions would be provided indicating the effective amount required to prevent skinning without significantly affecting other properties of the paint such as drying time and film hardness.

Another aspect is the method whereby the antioxidant, or a composition containing such antioxidant, can be stirred into the paint subsequent to its initial use and preferably each time the paint has been in use, the order to provide sufficient concentration of antioxidant at the paint/air interface. This method, however, is likely to result in relatively large quantities of antioxidant being required compared with the previous method, thereby increasing the likelihood of the paint becoming overloaded with antioxidant. Therefore more complex instructions and careful monitoring of the antioxidant would be needed to guard against the possibility of the paint being affected adversely with respect to such properties as viscosity, drying time and film hardness.

The process of the present invention can utilize any suitable antioxidant which is readily vaporisable and effective in the vapour phase, but we have found that preferably butyraldoxime and particularly preferably methyl ethyl ketoxime should be utilized as the antioxidant.

The antioxidant may be either utilized

alone or in combination with one or more solvents or liquid chemicals therefor.

According to a further aspect of the present invention, there is provided a composition for at least the substantial prevention of the formation of skin on the surface of a paint contained in a container which has been initially used, comprising an antioxidant together with one or more suitable solvents therefor.

The preferred antioxidant is butyraldoxime and particularly preferably methyl ethyl ketoxime, although any other suitable antioxidant may be utilized. The preferred solvent may be selected from one or more of dipentene, an alcohol, particularly *n*-butanol and white spirit. Dipentene is of assistance in preventing oxidation/polymerisation by providing a blanketing vapour at the paint/air interface. *n*-Butanol is useful in discouraging gelation tendencies in paints which have been subject to prolonged usage, and is also useful in assisting the prevention of "solvent shock" which could result in components of the paint kicking out of solution.

The antioxidant and the one or more solvents associated therewith are generally completely miscible with one another and simple agitation is generally the only manufacturing process required.

Preferred compositions in accordance with the invention are as follows:—

70	Constituent	Preferred Range	Particularly preferred value
	Methyl ethyl Ketoxime	10—90% by volume	25% by volume
	Dipentene	up to 60% by volume	10% by volume
75	<i>n</i> -Butanol	up to 20% by volume	5% by volume
	White Spirit	up to 90% by volume	60% by volume

The composition of the present invention will preferably be provided in a suitable container for example a bottle, sachet or capsule and instructions provided thereon to indicate to the user the method of application. For the processes whereby the composition is deposited upon the surface of the paint, preferably after each time the paint has been in use, the instructions will also indicate the effective amount required to prevent skinning without unduly affecting other properties of the paint such as drying time and film hardness.

It is particularly preferred to utilize a composition in accordance with the present invention not only because of the aforementioned beneficial effects of certain solvents but also because the antioxidant is only required in relatively small quantities, and if used on its own may prove difficult

for a user to utilize correctly. The composition of the present invention provides sufficient volume to more easily gauge the treatments required and ensures that the correct amount of antioxidant, which is of an expensive nature, is added in an economical manner.

It is also possible to use an antioxidant composition in gel or solid form, which is vaporisable and effective in the vapour phase.

The present invention is also applicable to small and large containers alike. Thus whilst the invention has been specifically described in relation to paint tins or cans, it is also applicable to the prevention of skin formation on the surface of dip tanks and large open containers of paint.

According to another aspect of the invention there is provided a further process

whereby wet painting apparatus such as dip tanks, open containers of paint and the like may be enclosed or partly enclosed within a housing, or envelope for instance of plastics material. The chemical or chemical composition may be located in a separate container within or without the housing or envelope to provide an effective vapour system within said housing or envelope thus preventing hardening of the paint or the formation of a skin on the surface of the paint therein. The preferred method for supplying the vapour would be by means of a vaporising wick or pad of suitable surface area located within said housing or envelope. Alternatively the vapour could be obtained directly from the surface of the liquid chemical or chemical composition located within said housing or envelope and having sufficient surface area to provide an effective vapour concentration.

The invention will be illustrated but in no way limited by the following examples.

Example 1

A medium skin was removed from an old one pint tin of pink Dulux (Registered Trade Mark) Gloss paint, the tin being approximately two thirds empty. 2 ml. of terebine driers was added and stirred in. A felt pad $1\frac{1}{4}$ " diameter \times $\frac{1}{4}$ " deep was soaked with the particularly preferred composition of the invention and attached to the underside of the lid by means of a magnet. Paint was smeared around the rim to help seal the lid. Two months later, the paint was found to be in a skin free condition after several previous inspections.

Example 2

A used $2\frac{1}{2}$ litre tin of Valspar (Registered Trade Mark) Gloss, New Gardenia, had approximately 1" depth of paint remaining in the tin after having been used on at least six previous occasions. 5 ml. of the particularly preferred composition of the invention was dropped onto the surface of the paint without stirring and the lid resealed. When opened 5 months later the paint was found to be completely free of skin. The paint was applied to a metal panel and dried hard overnight.

It will thus be seen that by utilizing the process, the composition and the apparatus in accordance with the invention at least substantial prevention of the formation of skin on the surface of a paint contained in a container, subsequent to its initial use, can be obtained.

The present invention is applicable to all oil bound air drying paints, varnishes, coatings, sealers and putty which dry by a process of oxidation/polymerisation.

It will thus be seen that by utilization of the process, composition and apparatus in

accordance with the present invention, the substantial prevention of the formation of a skin on the surface of a paint or related material can be attained. 65

WHAT WE CLAIM IS:—

1. A process for the prevention, or at least substantial prevention, of the formation of a skin upon the surface of a paint or related material which dries by a process of oxidation/polymerisation within a container, subsequent to its initial use and irrespective of the amount of paint or related material within the container, comprising supplying and maintaining in the air space above the paint or related material a sufficient concentration of vapour of an antioxidant which is effective in its vapour phase. 70 75 80

2. A process as claimed in claim 1, in which the antioxidant is supplied in the form of a liquid, which will adequately vapourise.

3. A process as claimed in claim 1 or 2, in which the antioxidant is utilized together with one or more solvents or liquid chemicals therefor. 85

4. A process as claimed in any one of claims 1, 2 or 3, in which the antioxidant, or a composition containing such antioxidant is incorporated into a pad or like device which is suspended in the air spaced above the paint or related material. 90

5. A process as claimed in any one of claims 1, 2 or 3 in which the antioxidant, or a composition containing such antioxidant, is located separate from the paint or related material in one or more dishes or housings. 95

6. A process as claimed in claim 2 or 3, in which the liquid antioxidant, or a composition containing such antioxidant, is deposited directly onto the surface or a portion of the surface of the paint or related material and is left thereon without mixing. 100 105

7. A process as claimed in claim 2 or 3, in which the liquid antioxidant is deposited onto the surface of the paint or related material and is then stirred thereinto.

8. A process as claimed in any preceding claim, in which the antioxidant is selected from ketoximes and/or aldoximes. 110

9. A process as claimed in claim 8, in which said antioxidant is methyl ethyl ketoxime or butyraldoxime. 115

10. A process as claimed in any preceding claim, substantially as hereinbefore described.

11. A device when used in the process of claim 1, for use in a paint or related material container, said device having an antioxidant, or a composition containing such antioxidant, thereon or therein for the prevention or at least substantial prevention of a skin upon the surface of a paint or related material which dries by a process of oxidation/polymerisation within said 120 125

- container, and said device being locatable above or partly above the surface of the paint or related material.
- 5 12. A device as claimed in claim 11, in the form of one or more pads, each said pad, in use, providing sufficient surface area to allow adequate vaporization of the antioxidant to take place.
- 10 13. A device as claimed in claim 12, in which the pad is made of felt, absorbent paper, foamed plastics material or other suitable absorbent material.
- 15 14. A device as claimed in claim 13, in which said pad is attachable to the lid of said container by means of a magnet or suction cup.
- 20 15. A device as claimed in claim 11, in the form of one or more dishes or housings locatable above or partly above the surface of the paint or related material, allowing vaporization to take place directly from the surface of the liquid therein.
- 25 16. A device as claimed in claim 15, in which each said dish or housing is provided with a wick or pad arrangement to permit vaporization to take place from such wick or pad.
- 30 17. A device as claimed in any one of claims 11 to 16 substantially as hereinbefore described.
18. A composition when used in the process of claim 1 for at least the substantial prevention of the formation of skin on the surface of a paint or related material which dries by a process of oxidation polymerisation contained in a container, subsequent to its initial use, comprising an antioxidant selected from methyl ethyl ketoxime or butyraldoxime together with one or more solvents therefor, said solvents being selected from dipentene, an alcohol, or white spirit.
19. A composition as claimed in claim 18, comprising 10—90% by volume of methyl ethyl ketoxime, up to 60% by volume of dipentene, up to 20% by volume of *n*-butanol and up to 90% by volume of white spirit.
20. A composition as claimed in claim 19 comprising 25% by volume methyl ethyl ketoxime, 10% by volume dipentene, 5% by volume *n*-butanol and 60% by volume white spirit.
21. A composition as claimed in claim 18, 19 or 20 substantially as hereinbefore described.

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