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[54] METHOD FOR REMOVING RESINOUS OR RUBBER DEPOSITS WITH ORGANIC PEROXIDES

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[51] **Int. Cl.** **B08b 3/08**

[58] **Field of Search** 134/2, 4, 29, 38, 22, 39; 252/94, 95, 96

[56] **References Cited**

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[57] **ABSTRACT**

Method for removing resinous and rubber films and other deposits from processing equipment or other coated surfaces comprising first applying to the deposit a catalyzed organic solvent solution of an organic peroxide, then activating decomposition of the peroxide-treated deposit by heating for about 15 minutes to about 4 hours at temperatures of about 100° to about 240° Fahrenheit, and simultaneously or subsequently subjecting the "scorched" deposit to the action of an alkaline aqueous cleaning solution.

9 Claims, No Drawings

METHOD FOR REMOVING RESINOUS OR RUBBER DEPOSITS WITH ORGANIC PEROXIDES

This invention relates to methods for removing undesirable resinous and rubber films or other deposits from processing equipment or other substrates coated therewith. In particular it relates to an improved two-step method which provides much faster removal of the undesired deposits.

In Kahn et al., U.S. Pat. No. 3,285,777 the patentees have disclosed a method for cleaning processing equipment with organic solvent solutions of up to about 20 percent by weight of an organic hydroperoxide and small amounts of a metallic compound to serve as peroxide decomposition catalyst. The method as disclosed requires continuous immersion of the contaminated surface for treatment times of 24 hours or more, in some cases up to as many as 6 days.

It is common practice in the paint stripping art to subject items to be stripped to alkaline stripping solutions, e.g., Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 14 (1967), pp. 490–491 and references cited at pages 492 and 493; and Goldsmith et al., U.S. Pat. No. 3,410,805. The disclosures of Kirk Othmer and Goldsmith et al., are hereby incorporated herein by reference.

It has now been discovered that the cleaning method suggested by Kahn et al., can be improved and greatly accelerated by a modification thereof and a sequential or simultaneous combination with a treatment with aqueous alkaline cleaning solutions, especially highly alkaline solutions of the type known in the paint stripping art.

Accordingly, the present invention provides a rapid efficient method for removing resinous and rubber deposits from substrates (e.g., processing equipment) to which they are adhered by applying to the deposit a solution of a mild organic peroxide and a metal soap catalyst in an organic solvent, thereafter heating the peroxide-treated deposit at an elevated temperature for a short time to at least partially decompose ("scorch" the deposit and then simultaneously or subsequently subjecting the scorched deposit to an aqueous alkaline cleaning solution to strip the scorched deposit from the substrate. Total treatment time required to remove the deposit can be reduced to as little as 30 minutes or so and seldom if ever exceeds about 1 hour although times up to about 4 hours are sometimes desirable.

The method of this invention is applicable to the removal of virtually any resinous or rubber film or other deposit. Among those to which the invention can be applied are the organic deposits described in the Kahn et al patent, as well as undesired deposits of olefin polymers and copolymers, vinyl and vinylidene polymers and copolymers, and various natural and synthetic rubbers; e.g., polyethylene, polypropylene, polybutadiene, polyvinylchloride, polyvinyl acetate, Neoprene, cured natural rubber, cured synthetic rubbers, and the like.

The organic peroxide solutions used in the initial step of the method of this invention have the following composition:

	Weight Percent	
Ingredient	Operable	Preferred
Organic solvent	40 to 89	about 65
Peroxide	10 to 50	about 30
Metal catalyst	1 to 10	about 5

The organic solvent may be any organic liquid which is substantially inert with respect to the peroxide and which dissolves substantially all of the peroxide and metal catalyst compound. Operable solvents include aliphatic, alicyclic and aromatic compounds and mixtures thereof including for example, hexane, heptane, isooctane, toluene, benzene, kerosene, benzene, monochlorobenzene and the like.

The peroxides used in the practice of the invention are mild organic peroxides, i.e., those which have a half life (measured in dilute benzene solutions) greater than about 1 hour at 212° Fahrenheit and which thus can (although not recommended for long periods) be handled and stored at ambient temperatures without excessive danger. Representative examples of

such peroxides are di-(tertiary-butyl) peroxide, tertiary-butyl perbenzoate, benzoyl peroxide, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(tertiary-butylperoxy) hexane (Wallace and Tiernan's Lupersol 101), 2,5-dimethyl-2,5-di(tertiary-butylperoxy) hexyne-3 (Wallace and Tiernan's Lupersol 130) and the like. The preferred peroxide is di-(tertiary-butyl) peroxide.

The metal catalyst used in the practice of this invention is a heavy metal salt of a higher fatty acid which is soluble in the chosen organic solvent. These salts are those commonly used as driers in the paint, varnish, printing ink and linoleum industries and have the formula

$$(RCOO)_x Me$$

wherein x represents the valence of the metal Me; Me is a metal of the group consisting of cobalt, copper, zinc, aluminum, iron, lead, manganese, calcium, barium, lithium, magnesium, or mixtures thereof, and (RCOO—) is the residue of an organic aliphatic, alicyclic or aromatic monocarboxylic acid having from about 7 to about 24, preferably about 18, carbon atoms. (See Kirk-Othmer, Encylcopedia of Chemical Technology, Second Edition, Volume 7 (1965), pp. 272–283).

Suitable metal salts include the cupric, zinc, cobalt, aluminum, iron, manganese, calcium, barium, lithium or magnesium. Salts of naphthenic, linoleic, linoresinic, palmitic, oleic, stearic, lauric, rosin, tall oil, 2-ethylhexoic, 3,5,5-trimethylhexoic or neodecanoic acids. The preferred metal catalyst salts are the naphthenates, especially cobalt naphthenate.

The peroxide solution may be applied to the deposit to be treated by any suitable procedure, e.g., spraying, dipping, brushing or the like. In the practice of the present invention immersion for prolonged periods of time is not necessary or desirable. The peroxide solution or the active ingredients of the peroxide solution, i.e., the peroxide and metal catalyst, are permitted to remain in contact with the deposit for a short period of time (e.g., 5 to 20 minutes) and the treated deposit is then heated to accomplish scorching.

Heating is carried out for a period of from about 15 minutes to about 4 hours at temperatures of from about 100° to about 240° Fahrenheit, preferably from about 160° to about 220° Fahrenheit. Of course, the time and temperature of the heat treatment will vary with the deposit involved and the amount thereof, the particular peroxide treatment solution used, and other like factors. In almost all cases satisfactory results are achieved with heating times of 1 hour or less.

The scorched deposit is subjected to the action of an aqueous alkaline cleaning solution to remove it from the surface to be cleaned. This removal step may be performed subsequent to or simultaneously with the scorching step. Wherever possible the steps are performed simultaneously, thus reducing the overall time required to complete the overall removing process. The two steps are conducted sequentially in the presently preferred embodiment of the invention. It is to be understood, however, that simultaneous performance of the scorching and removing steps has been demonstrated to be operable and is thus included within the scope of the invention.

The aqueous alkaline solution used in the final step of the present invention can be a solution of an alkali metal hydroxide alone or of a mixture of an alkali metal hydroxide with minor proportions (e.g., from about 5 to about 30 weight percent of the total alkaline solids) of one or more other alkaline salts such as alkali metal carbonate, phosphate, metasilicate or the like. The working solutions of alkali strippers will usually have a dissolved solids concentration of about 5 to about 25 percent, preferably 10 to 20 percent by weight, corresponding roughly to about 0.5 to 3, preferably 1 to 2, pounds of solids per gallon of water. However, any alkaline cleaner which will leave a clean surface can be used and the exact formulation is unimportant to the present invention as long as the solution contains sufficient caustic soda or caustic potash to provide a

2.0 to 50.0 percent (by weight) solution of free caustic soda or caustic potash, as part of the dissolved solids, any of the usual co-additives known in the prior art. Some of the typical co-additives are disclosed, for example, in the aforecited Volume 14 of Kirk Othmer Encyclopedia of Chemical Technology, Second Edition.

The invention will be further understood from the following illustrative, non-limiting examples.

EXAMPLE 1

In this Example the peroxide solution comprised 60 weight percent kerosene solvent, 30 weight percent di-(tertiary-butyl) peroxide and 10 weight percent cobalt naphthenate catalyst.

To demonstrate the present invention a 3 inch by 1 inch steel test panel was coated with a Neoprene latex and the coating was allowed to dry for 24 hours at room temperature. A film of the above peroxide solution was sprayed on the Neoprene coating and the panel was immediately immersed in a hot (200° Fahrenheit) stripper solution comprising 2.5 percent caustic potash, 1.8 percent cresylic acid, 0.5 percent of a sequesterant and balance water. The panel was retained in the hot stripper solution for 20 minutes after which it was removed and permitted to cool to room temperature.

The Neoprene coating was observed to be severely degraded and partially stripped from the test panel at the time of removal from the hot stripper solution. The Neoprene still remaining on the panel was easily removed by manual stripping.

In a repeat of the foregoing procedure, equally good results were obtained with a like peroxide solution in which the solvent was orthodichlorobenzene instead of kerosene.

EXAMPLE 2

In this example the peroxide solution contained 63 weight percent orthodichlorobenzene, 32 weight percent di-(tertiary-butyl) peroxide and 5 weight percent cobalt naphthenate. The aqueous cleaning solution contained 94.5 weight percent water, 2.5 weight percent potassium hydroxide, 1 weight percent of a sequestrant and 2 weight percent couplers (i.e., water soluble or water miscible cosolvents).

The test sample was a 3 inch by 1 inch steel panel coated with a polyvinylacetate latex and dried at room temperature for 24 hours. The panel was dipped briefly in the above peroxide solution, and then allowed to drain for 10 minutes at room temperature. The panel was then immersed in the above alkaline cleaning solution at 190° Fahrenheit for 30 minutes.

Results were like those obtained in Example 1, with portions of the polymer coating removed and the remainder badly degraded and readily removed manually after removal of the test panel from the hot aqueous cleaning solution.

When attempts were made to clean like test panels with the aqueous alkaline cleaner solution alone, there were no signs of any kind of attack or removal of the resinous deposit.

EXAMPLE 3

In this example the peroxide solution was the same as the one used in Example 2 except for the substitution of tertiary-butyl perbenzoate for the di-(tertiary-butyl) peroxide.

A portion of an automobile tire mold bearing a black film of cured tire compound was dipped briefly in the peroxide solution and then allowed to drain for 10 minutes at room temperature. The peroxide treated piece was then heated in a hot air oven for 30 minutes at 120° Fahrenheit.

After cooling to room temperature the piece was manually cleaned by rubbing with a cloth in an aqueous solution of a mild dishwashing compound. Some of the cured rubber compound remained in the mold crevices but the accessible undesired deposits were removed.

Previous attempts had been made to remove this rubber deposit by using mildly alkaline products, as well as water miscible solvent products containing over 50 percent orthodichlorobenzene both with and without the aid of ultrasonics. These attempts showed no effect on the rubber deposit.

EXAMPLE 4

The peroxide solution was identical to the one used in Example 3. The aqueous alkaline cleaning solution contained 3.0 weight percent sodium hydroxide and 5.0 weight percent sodium carbonate, together with other typical coadditives.

The substrate to be cleaned was a closed 6,000 gallon steel tank coated with a thin film of a dried adhesive. The identity of the adhesive was not known. The contaminated tank surface was sprayed with one-half gallon of the peroxide solution and then heated with steam under atmospheric pressure for 30 minutes. Immediately after this heat treatment the coated tank surfaces were hit for 1 hour with a pressurized spray (150 pounds per square inch gauge) of the above alkaline cleaning solution pre-heated to 140° Fahrenheit.

The tank was completely clean after the foregoing treatment.

Previous attempts to clean the tank with the alkaline product alone only served to further harden the coating of adhesive deposit and render more difficult the hand scraping operations then in use.

What is claimed is:

1. Method for removing undesirable resinous or rubber deposits from substrates bearing the same comprising:
   a. first applying to the deposit a solution of an organic peroxide and a peroxide decomposition catalyst in an organic solvent;
   b. then activating decomposition of the peroxide treated deposit by heating at a temperature of from about 100° to about 240° Fahrenheit for a period of from about 15 minutes to about 4 hours;
   c. simultaneously with or subsequent to step (b), subjecting the deposit to the action of an aqueous alkaline cleaning solution to remove at least a portion of the undesirable deposit from the substrate.

2. Method of claim 1 wherein the undesired deposit is Neoprene rubber.

3. Method of claim 1 wherein the undesired deposit is poly(vinyl acetate).

4. Method of claim 1 wherein the undesired deposit is cured automobile tire compound.

5. Method of claim 1 wherein the aqueous alkaline cleaning solution employed in step (c) comprises at least about 2 percent by weight of free alkali metal hydroxide.

6. Method of claim 5 wherein the alkali metal hydroxide is sodium hydroxide.

7. Method of claim 1 wherein the peroxide employed in step (a) is di(tertiary-butyl) peroxide or tertiary-butyl perbenzoate.

8. Method of claim 7 wherein the peroxide decomposition catalyst is a heavy metal salt of a fatty acid having from about seven to about 24 carbon atoms.

9. Method of claim 8 wherein the metal salt is cobalt naphthenate.

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