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## (54) Method for improving the adherence to radiation cured coatings.

(57) Method for improving the adherence to radiation cured coating, especially one based on multifunctional acrylates or epoxides, which may be used as protective overlayer in a radiographic screen comprising treating the coating with a composition having a pH of at least 7 preferably at least 10, so that the surface free energy of the radiation cured coating increases to at least about 37 mN/m, preferably to at least about 45 mN/m.

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The present invention relates to radiation cured coatings, especially those based on multifunctional acrylates and epoxides, and particularly to radiation cured coatings in radiographic screens, more particularly to a method for improving the adherence to radiation cured coatings.

Radiation cured coatings are formed from polymerizable formulations, usually mixtures of unsaturated prepolymers diluted with monomers or fluid oligomers, that are cured (polymerized) by subjection to electromagnetic radiation such as ultraviolet (UV) radiation (wavelength 150 to 450 nm, 4-6 eV) or accelerated electron beams (EB) (150 to 350 keV). These two kinds of high energy radiation, upon interaction with organic matter, give rise to the formation of free radicals, thereby initiating the chain-reaction polymerization. The mechanisms of propagation and termination are similar, whether UV light or EB is used, only the mechanism of initiation being different in the two processes. UV curable formulations contain a photoinitiator which produces initiating radicals upon UV exposure; EB curing is initiated through the indiscriminate interaction of accelerated electrons with organic matter resulting in chemical bond rupture.

The different types of radiation curable systems commonly used are unsaturated polyester resins, thiol polyene systems, multifunctional acrylates and epoxides. The latter system relates to cationic polymerisation while the former systems relate to free radical polymerisation.

Current commercial applications of radiation curable systems include protective and decorative coatings on wood and particleboard, metal (e.g., beverage cans), plastic (e.g., vinyl flooring), paper and board (e.g., packaging, paperback books), inks, photopolymers (e.g., photoresists, printing plates), adhesives.

A survey of radiation curable compositions and their applications is given in "Grundlagen der Strahlungshärtung" by Degussa AG (May 1980), in Farbe + Lack, 9/1985, page 812-815 by W. Brushwell, in Radiation Curing, February 1986, page 4-10 by G.W. Gruber, in Polymers Paint Colour, Oct. 5th 1988, page 81-89 by C. Decker, in Farbe + Lack, 5/1989, page 324-326 by H. Sellmer, and in the Lectures Notes of the Symposium on Radiation Curing organized by The Center for Professional Advancement in Amsterdam, 3th-5th October 1988.

Radiation cured coatings are also used as protective coatings for radiographic screens; the term radiographic screen covering conventional X-ray conversion screens as well as stimulable X-ray conversion screens.

In conventional radiography, particularly medical radiography, an X-ray image is obtained by irradiating X-ray transmitted through a subject on an X-ray conversion screen containing on a support a layer of fluorescent phosphor which absorbes X-rays and converts them into visible light and/or ultraviolet radiation when struck by X-rays, irradiating visible light to a film coated with a silver halide emulsion layer and consequently developing the film. The X-ray films which are used generally comprise a transparant film support coated on each of its faces with a silver halide emulsion layer. Two X-ray conversion screens are usually employed, one positioned on each side of the double-side coated film; the film together with the two screens is encased in a suitable cassette. Combinations of single emulsion films with single screens are often used in high definition applications (extremities, mammography).

In recent years, methods producing images directly from the phosphor layer without use of a film coated with a silver salt have been devised. A description of such methods can be found in US 3859527, US 4239968, US 4258264, US 4654533 and US 4710626. In such a method, X-ray radiation transmitted through a subject is irradiated on a stimulable phosphor layer of a stimulable X-ray conversion screen to accumulate radiation energy corresponding to the radiation transmission degrees at respective portions of the subject and forming a latent image, then the stimulable phosphor layer is scanned with a stimulating excitation light, thereby releasing the radiation energy stored at the respective portions as light emission, and subsequently an image is obtained according to the optical signals depending on the intensity of the emitted light. The image may be processed and the obtained final image may be reproduced as a hard copy or reproduced on CRT. The stimulable phosphor sheet does not serve to finally record image information, but only stores the information temporarily to provide the image or the like on an independently prepared final recording medium. Accordingly, the stimulable phosphor sheet can, after stimulation erased, be repeatedly used.

Traditionally, (stimulable) X-ray conversion screens comprise, in order, a support, an active layer comprising a (stimulable) fluorescent phosphor dispersed in a suitable binder and a protective topcoat or abrasion layer coated over the active layer to protect said active layer during use.

Since each radiographic screen is used frequently, it is important to provide them with an adequate topcoat effectively protecting the active layer from physical and chemical deterioration. This is particularly important in stimulable radiographic screens where the screen is not encased in a cassette but is used and handled as such. Use of a radiation curable coating as protective toplayer in a (stimulable) X-ray conversion screen as described in, e.g., EP 209358 and JP 86/176900, has provided satisfactory results.

A perceived disadvantage of radiation cured coatings, especially those based on multifunctional acrylates and epoxides, is the poor adherence to said coatings. This is important where for example in packaging context package information is produced by a printing process using UV curable inks and an overprint coating is used to protect the ink from scuffing and pick-off; the adherence of said overprint coating on said UV cured ink being poor. Also in radiographic screens this poor adherence represents a problem where one wants to print some information e.g. regarding the type and speed of the screen, the manufacturing number or a bar code label on the radiation cured protective coating; the ink used for printing said information does not adhere sufficiently to the radiation cured coating and neither does an overlayer used to protect the ink.

This poor adherence applies to all kinds of materials to be adhered onto the radiation cured coatings; the most extreme case being the poor autohesion, i.e. the adhesion of a radiation curable coating to a radiation cured coating.

In order to achieve adequate adhesion to a polymeric substrate it is often necessary to carry out a surface pretreatment. A description of various surface pretreatment for plastics is given in "Surface Analysis and Pretreatment of Plastics and Metals", Edited by D.M. Brewis, Applied Science Publishers Ltd., London, 1982. Pretreatment methods for improving the adhesive characteristics of polyolefin surfaces, such as treatment by oxidising solutions (etchants) and electrical ('corona') discharge treatment, applied to radiation cured coatings do not improve the adherence thereto.

It is an object of the present invention to improve the adherence to radiation cured coatings, especially those based on multifunctional acrylates and epoxides.

It is another object of the present invention to improve the printability of radiation cured topcoats of radiographic screens.

Other objects will become apparent from the description hereinafter.

The present invention provides a method for improving the adherence to radiation cured coatings which method comprises treating the radiation cured coating with a composition having a pH of at least 7 so that the surface free energy of the radiation cured coating increases to at least about 37 mN/m, preferably to at least about 45 mN/m.

The method used for determining the surface free energy of the coating is the measurement of the contact angle which a liquid makes with the coating, i.e. the angle between the liquid/vapour interface and the liquid/solid interface from the point of three phase contact of a drop of liquid resting on the surface of the coating at equilibrium.

A review of the methods of contact angle measurement, together with an analysis of the relevant thermodynamic equations is given by D.G. Rance in "Surface Analysis and Pretreatment of Plastics and Metals", Edited by D.M. Brewis, Applied Science Publishers, London, 1982, page 121-152 and by R.J. Good and A.W. Neumann in "Surface and Colloid Science", Vol. 11, Edited by R.J.Good and R.R. Stromberg, Plenum Press, New York, 1979, page 1-91.

The contact angle may be obtained by drawing a tangent to the profile at the point of the three phase contact, the drop profile being enlarged either by image projection or photography. It may be measured directly using a telescope fitted with a goniometer eyepiece, or indirectly by measuring the angle at which light from a point source is reflected from the surface of a liquid drop at its point of contact with the solid. Another useful method of indirect determination is measurement of the drop dimensions, i.e. the height and the base diameter of the drop. It may be appropriate to determine the contact angle as the mean of the advancing and receding contact angle, this method being described by H. Bracke, F. De Bisschop and P. Joos in Progr. Colloid Polym. Sc., no. 76 (1988), page 251-259.

The relevant equation to be used for calculating the surface free energy of the coating ( $_s$) being the sum of surface free energy due to dispersion interactions ( $^d_s$ ) and surface free energy due to polar interactions ( $^p_s$ ) out of the measurement of the contact angle ( ) is the following:

$$_s(1 + \cos\ \ ) = 2(\,^d_s\ ^d_l)^{0.5} + 2(\,^p_s\ ^p_l)^{0.5}$$

wherein $^d_l$ and $^p_l$ are the disperse, respectively polar components of the surface free energy of the liquid.

The measurement of equilibrium contact angles of two liquids of which ${}^{d}_{l}$ and ${}^{p}_{l}$ are known provide all the information needed to solve two equations constructed using the above equation and thus to obtain ${}^{d}_{s}$ and ${}^{p}_{s}$.

Values of ${}^{p}_{s}$ and ${}^{d}_{s}$ for the coating can also be determined from contact angles of a number of well-characterised liquids by a graphical method.

Preferably, a treating composition having a pH greater than 10 is used. Using a composition having a pH less than 10 leads to a prolonged time of treatment for the desired surface free energy to be obtained.

Using a composition having poor intrinsic physical spreading capacity also leads to an increased time of treatment for a sufficient proportion of the surface of the radiation cured coating acquiring molecular contact with the treating liquid. For this purpose, a spreading agent such as a surfactant or alcohols may be added to the treating composition in order to lower the surface tension of the composition.

The treating composition can be applied by rubbing the surface of the coating with the composition or by dipping the coating in the composition. Depending on the time of contact necessary for the surface free energy of the coating to be increased to the desired level, the coating is rubbed a few times or is dipped in the composition for a longer period of time; not only the time of contact in wet state is important but also the contact time in dry state.

In the event of the radiation cured coating being a protective topcoat of a radiographic screen to be printed with, for example, some manufacturing information, the ribbon carrying the printing ink may be treated on the printing side with the composition of the present invention prior to printing, in an on-line or off-line configuration, so that simultaneously treating and printing of the radiation cured topcoat is carried out while the ribbon and the topcoat are in contact with each other during printing.

Examples of alkaline compounds for use according to the present invention include anorganic bases such as LiOH, KOH, NaOH, $Ca(OH)_2$, $Mg(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, $Pb(OH)_2$, $Zn(OH)_2$, AgOH, $NH_4OH$, $NH_2NH_2$ and organic bases such as primary, secundary and tertiary amines, quaternary ammonium hydroxide, ureum, alkane diamines, hydroxy alkane amines, piperidine, morpholine, p-amino pyridine. Compounds forming a base in situ can also be used, e.g., sodium-, potassium- and barium alkylate, $Na_2CO_3$, $Na_2SO_3$.

Preferred alkaline compounds are alkali and earth alkali metal hydroxides, preferably $Ba(OH)_2$ and quaternary ammonium hydroxides, preferably $(CH_3)_4NOH$.

Preferably, a surfactant such as $C_7F_{15}COONH_4$ or alcohols such as methanol, ethanol and isopropylalcohol are added to the aqueous alkaline composition in order to improve the spreading of the treating composition onto the surface of the radiation cured coating.

The composition is applied to the radiation cured coating by rubbing once or several times or by dipping the coating in the composition for some time. Thereafter the composition is allowed to interact with the surface for some time in wet state and for some time in dry state. The intensity of applying and the time of interaction necessary to obtain the desired improvement in adherence depend on the pH of the composition, the spreading capacity of the composition, the nature of the radiation cured coating and the nature of the substrate to be adhered.

The joint strength between an adhered substrate and a treated radiation cured coating increases with an increase of the pH of the treating composition, with an increase in the spreading capacity of the treating composition, with an increase in the time of treatment and with an increase of the treatment temperature.

A typical radiation curable formulation contains a prepolymer, a reactive diluent monomer or oligomer and in the case of an UV curable formulation a photoinitiator. The usual amounts of these primary components are 30-100 % by weight for the prepolymer, 0-70 % by weight for the reactive diluent and 0-10 % by weight for the photoinitiator.

In addition to these primary components additives may be added in an amount of 0-2 % by weight. As additives may be used surfactants, waxes, defoamers, plasticizers and stabilizers. Pigments may be added in an amount of 0-60 % by weight.

As the prepolymer or oligomer having two or more unsaturated double bonds, there may be exemplified the following: unsaturated polyesters; modified unsaturated polyesters such as urethane modified unsaturated polyester, acrylic urethane modified unsaturated polyester, and a liquid unsaturated polyester having an acrylic group at a terminal; acrylic polymers such as polyesteracrylate, epoxyacrylate, siliconeacrylate and urethaneacrylate; butadiene series polymer; epoxy series polymer such as polyglycidyl ether of aliphatic polyol, bisphenol A (or F, S) diglycidyl ether, dicarboxylic acid epoxycyclohexylalkyl and epoxide containing one or two or more cyclopenteneoxide groups; polythiol polyene resin.

The radiation curing type resin mentioned above may be employed alone or as a mixture of two or more.

Diluent monomers are used in radiation curable formulations to reduce the viscosity and to increase flow characteristics. These monomers participate in the free radical curing process. As the abovementioned reactive diluent affecting to reduce the viscosity of the composition and enhance the radiation-curing rate, there may be exemplified the following: mono-functional monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, n-hexyl acrylate, lauryl acrylate, etc; di-functional monomers such as 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, silicone diacrylate, neopentylglycol, 1,4-butanediol diacrylate, ethyleneglycol diacrylate, polyethyleneglycol diacrylate, pentaerythritol diacrylate, divinylbenzene, etc.; tri- or more-functional monomers such as trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, an acrylate of ethylenediamine, aliphatic and aromatic urethane acrylates, etc.

If ultraviolet irradiation is employed as a means for curing, there is added, photoinitiator which is a catalyst to initiate the polymerization by absorption of ultraviolet ray energy, and further added photosensitizer for accelerating the effect of the photoinitiator by transferring energy and forming free radicals by interaction.

As the abovementioned photoinitiator, carbonyl compounds are frequently employed, for example, benzoin ether series compounds such as benzoin isopropyl, isobutylether; benzil ketal series compounds; ketoxime esters; benzophenone series compounds such as benzophenone, o-benzoylmethylbenzoate; acetophenone series compounds such as acetophenine, trichloroacetophenone, 1,1-dichloroacetophenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone; thioxanthone series compounds such as 2-chlorothioxanthone, 2-ethylthioxanthone; and compounds such as
2-hydroxy-2-methylpropiophenone,
2-hydroxy-4'-isopropyl-2-methylpropiophenone,
1-hydroxycyclohexylphenylketone; etc.

Moreover, as a photoinitiator, particularly, for epoxy series polymers, there may be useful an aromatic onium salt, namely, a diazonium salt such as a diazonium salt of a Lewis acid; a phosphonium salt such as a hexafluorophosphoric triphenylphenacylphosphonium salt; a sulfonium salt such as a tetrafluoroboric triphenylsulfonium, hexafluoroboric triphenylsulfonium; and an iodonium salt such as a chlorodiphenyl iodonium; etc. As the others, sulfuric compounds, azo compounds, halogen compounds, organic peroxides, etc. may be employed as photoinitiator.

The abovementioned photopolymerization initiator may be used alone or as a mixture of two or more.

As the examples of the photosensitizer, there may be mentioned amine, nitrile and compounds of sulfur, phosphor, nitrogen, chlorine, etc.

Apparatus and methods for curing the curable coating compositions described herein by subjecting them to suitable forms of radiation are well known, and any suitable radiation curing process can be used. For example, the coating can be cured by subjecting it to ultraviolet radiation of suitable intensity from medium pressure mercury arc lamps or other sources of ultraviolet radiation. High energy ionizing radiation such as X-rays, gamma rays, beta rays and accelerated electrons can also be used to accomplish curing of the coating. Typically, the radiation used should be of a sufficient intensity to penetrate substantially all the way through the coated layer. The total dosage employed should be sufficient to bring about curing of the radiation curable coating composition to form a solid layer.

UV radiation is better suited to non-pigmented or slightly pigmented systems having relatively thin films to allow full penetration of the irradiation. For high pigmented coatings, polymerization is best achieved by electron beam curing because EB curing can penetrate through thicker and opaque films.

UV irradiation is usually carried out employing medium pressure mercury arcs or pulsed xenon arcs. These ultraviolet sources usually are equipped with a cooling installation, an installation to remove the produced ozone and a nitrogen inflow to exclude air from the surface of the product to be cured during radiation processing. An intensity of 40 to 120 W/cm in the 200-400 nm region is usually employed. An example of a commercially available ultraviolet source is IST supplied by Strahlentechnik, Oberboihingen, W. Germany.

There are two types of electron beam accelerators: high energy scanner types and low energy linear-cathode types also called electrocurtain type accelerators. These accelerators are usually equipped with nitrogen inflow. A dose in the range of 0.01 to 10 megarads is employed. Examples of commercially available EB accelerators are PILOT 200 and CBI75/60/380 both supplied by Energy Sciences Inc., Geneva, Switzerland.

Curing periods may be adjusted to be very short by proper choice of radiation source, photoinitiator and concentration thereof, prepolymer and reactive diluent, distance between the radiation source and the product to be cured. Curing periods of about .1 second duration are possible, especially in thin film applications such as desired, for example, in coatings. For thicker cured products, curing periods up to 5 minutes, preferably 1-2 minutes, are operable.

An important application of radiation cured coatings is the formation of a protective overcoat on top of the phosphor layer of a radiographic screen.

A radiographic screen basically comprises a support and a phosphor layer provided thereon, said phosphor layer comprising a binder and a (stimulable) phosphor dispersed therein.

In the case of a conventional X-ray conversion screen the phosphor used is a fluorescent substance that emits ultraviolet radiation and/or visible light when struck by penetrating X-ray radiation.

The phosphor can be selected from a variety of well-known X-ray luminescent phosphors or phosphor particles taught by the prior art. The phosphors include, for example, calcium tungstate, zinc sulfide, zinc cadmium sulfide, zinc oxide and calcium silicate, zinc phosphate, alkali halides, cadmium sulfide, cadmium selenide, cadmium tungstate, magnesium fluoride, zinc fluoride, strontium sulfide, zinc sulfate, barium lead sulfate, barium fluorohalides, and mixtures of two or more of the above. The above phosphors may be activated with, for example, europium, silver, copper, nickel. Phosphors which are particularly suitable for use in high speed X-ray conversion screens are those selected from fluorescent substances containing elements with atomic number 39 or 57 to 71, which include rare earth elements such as yttrium, gadolinium, lanthanum and cerium. Particularly suitable are the rare earth oxysulfide and oxyhalide fluorescing materials activated with other selected rare earths e.g. lanthanum and gadolinium oxybromide and oxychloride activated with terbium, ytterbium or dysprosium, lanthanum and gadolinium oxysulfides activated with terbium, europium, or a mixture of europium and samarium, yttrium oxide activated with gadolinium, europium, terbium or thulium, yttrium oxysulfide activated with terbium or a mixture of terbium and dysprosium, yttrium tantalate doped with small amounts of terbium or strontium or lithium or a mixture thereof and activated with thulium, niobium, europium, gadolinium, neodymium. These and other rare earth fluorescent materials have been extensively described in the literature for which we refer, e.g., to EP 11909, EP 202875, EP 257138, DE 1282819, DE 1952812, DE 2161958, DE 2329396, DE 2404422, FR 1580544, FR 2021397, FR 2021398, FR 2021399, UK 1206198, UK 1247602, UK 1248968, US 3546128, US 3725704, US 4220551, US 4225653, also to K.A. Wickersheim et al. "Rare Earth Oxysulfide X-ray Phosphors", in the proceedings of the IEEE Nuclear Science Symposium, San Francisco, October 29-31, 1969, to S.P. Wang et al., IEEE Transactions on Nuclear Science, February 1970, p. 49-56, and to R.A. Buchanan, IEEE Transactions on Nuclear Science, February 1972, p. 81-83. A survey of blue light and green light emitting phosphors is given in EP 88820.

By using a plurality of phosphor layers of different composition or by using a radiographic screen containing a mixture of different phosphors a fluorescence over the whole visible spectrum can be obtained, so that such combination is particularly useful for recording with silver halide recording elements that have been made spectrally sensitive for light of the whole visible spectrum.

The stimulable phosphor used in a stimulable X-ray conversion screen refers to a phosphor which can exhibit stimulated fluorescence when irradiated with a stimulating excitation light after X-ray irradiation. From the viewpoint of practical use, the stimulable phosphor is desired to give stimulated emission in the wavelength region of 300 to 500 nm when excited with stimulating rays in the wavelength region of 400 to 900 nm. Alternatively, stimulable phosphors emitting around 600 nm, such as described in US 4825085, can be used. As the stimulable phosphor to be used, there may be mentioned, for example, those described in EP 304121, EP 345903, EP 353805, US 3859527, US 4236078, US 4239968, JP 73/80487, JP 73/80488, JP 73/80489, JP 76/29889, JP 77/30487, JP 78/39277, JP 79/47883, JP 80/12142, JP 80/12143, JP 80/12144 = US 4236078, JP 80/12145, JP 80/84389, JP 80/160078, JP 81/116777, JP 82/23673, JP 82/23675, JP 82/148285, JP 83/69281, JP 84/56479. The divalent europium activated alkaline earth metal halide phosphors and rare earth element activated rare earth oxyhalide phosphors are particularly preferred, because these show stimulated emission of high luminance.

The stimulable X-ray conversion screen may have a group of stimulable phosphor layers containing one or more stimulable phosphor layers comprising at least one of the stimulable phosphors as mentioned above. The stimulable phosphors to be contained in respective stimulable phosphor layers may be either identical or different.

The (stimulable) phosphors can be used in any conventional particle size range and distribution. It is generally appreciated that sharper images with less noise are realized with smaller mean particle sizes, but light emission efficiency declines with decreasing particle size. Thus, the optimum mean particle size for a given application is a reflection of the balance between imaging speed and image sharpness desired.

The (stimulable) phoshors are in the form of a layer applied to a support, or applied as a self-supporting layer or sheet.

While it is recognized that the (stimulable) phosphor layer does not have to contain a separate binder, in most applications the phosphor layers contain sufficient binder to give structural coherence to the layer. In general, the binders useful in the practice are those conventionally employed in the art and include proteins such as gelatin, polysaccharides such as dextran, gum arabic, and synthetic polymers such as polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polystyrene, polyester, etc. These and other useful binders are disclosed in US 2502529, US 2887379, US 3617285, US 3300310, US 3300311, US 3743833, RD 15444. A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate.

Usually the active layer contains (stimulable) phosphor particles in an extremely larger amount than a binder and is considerably thick from the viewpoint of sensitivity.

The ratio between the binder and the (stimulable) phosphor may be determined according to the characteristics of the aimed radiographic screen and the nature of the phosphor employed. Generally, the ratio therebetween is within the range of from 1:1 to 1:100 (binder:phosphor, by weight), preferably from 1:10 to 1:25.

The thickness of the (stimulable) phosphor layer, which may differ depending on the sensitivity of the radiographic screen to radiation, the kind of the (stimulable) phosphor, etc., may be within the range of from 10 to 1000 um, preferably from 50 to 500 um, more preferably from 150 to 250 um.

Two or more phosphor layers with different thickness and/or different binder:phosphor ratio and/or different phosphor particle size may be used.

Examples of the support material include plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; and papers sized with polyvinyl alcohol or the like. A plastic film is preferably employed as the support material.

The plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide or barium sulfate. The former is appropriate for preparing a high-resolution type radiographic screen, while the latter is appropriate for preparing a high-sensitivity type radiographic screen.

Examples of preferred supports include polyethylene terephthalate, clear or blue colored or black colored (e.g., LUMIRROR C, type X30 supplied by Toray Industries, Tokyo, Japan), polyethylene terepthalate filled with $TiO_2$ or with $BaSO_4$.

These supports may have thicknesses which may differ depending on the material of the support, and may generally be between 60 and 1000 um, more preferably between 80 and 500 um from the standpoint of handling.

The (stimulable) phosphor layer can be formed on the support, for instance, by the following procedure.

(Stimulable) phosphor particles and a binder are added to an appropriate solvent, and then mixed to prepare a coating dispersion comprising the phosphor particles homogeneously dispersed in the binder solution.

Examples of the solvent employable in the preparation of the coating dispersion include lower alcohols such as methanol, ethanol, n-propanol and n-butanol; chlorinated hydrocarbons such as methylene chloride and ethylene chloride; ketones such as acetone, butanone, methyl ethyl ketone and methyl isobutyl ketone; esters of lower alcohols with lower aliphatic acids such as methyl acetate, ethyl acetate and butyl acetate; ethers such as dioxane, ethylene glycol monoethylether; methyl glycol; and mixtures of the abovementioned compounds.

The coating dispersion may contain a dispersing agent to improve the dispersibility of the phosphor particles therein, and may contain a variety of additives such as a plasticizer for increasing the bonding between the binder and the phosphor particles in the phosphor layer.

Examples of the dispersing agent include ionic and nonionic well-known dispersing agents or combinations thereof, e.g., GAFAC RM 610 supplied by General Aniline and Film Company (GAF), New York, USA, polyoxyethylene (20) sorbitan monopalmitate and monolaurate, polymeric surfactant such as acrylic graft copolymer, PHOSPHOLIPON 90 supplied by Nattermann-Phospholipid GmbH, Köln, W. Germany, silane dispersing agents such as SILANE Z6040 supplied by Dow Corning Corporation, Midland, Michigan, USA or glymo 3-glycidyloxypropylmethoxysilane or organosulfate polysilanes, unsaturated p-aminamide salts and high molecular acid esters such as ANTI TERRA U 80 supplied by BYK-Chemie GmbH, Wesel, W. Germany, high molecular unsaturated polyesters. Dispersing agents are added in an amount of 0.05 to 10 % by weight as compared to the phosphor.

Examples of the plasticizer includes phosphates such as triphenyl phosphate, tricresyl phosphate and diphenyl phosphate; phthalates such as diethyl phthalate and dimethoxyethyl phthalate; glycolates such as ethylphthalyl ethyl glycolate and butylphthalyl butyl glycolate; and polyesters of polyethylene glycols with aliphatic dicarboxylic acids such as polyester of triethylene glycol with adipic acid and polyester of diethylene glycol with succinic acid.

The coating dispersion may also contain a filler (reflecting or absorbing) or may be colored by colorant capable of absorbing light within the spectrum emitted by the phosphor or capable of absorbing excitation light in the case of a stimulable X-ray conversion screen. Examples of colorants include Solvent Orange 71 (Diaresin Red 7), Solvent Violet 32 (Diaresin Violet A), Solvent Yellow 103 (Diaresin Yellow C) and Solvent Green 20 (all four supplied by Mitsubishi Chemical Industries, Japan), Makrolex Rot GS, Makrolex Rot EG, Makrolex Rot E2G, Helioechtgelb 4G and Helioechtgelb HRN (all five supplied by Bayer, Leverkusen, W. Germany), Neozaponfeuerrot G and Zaponechtbraun BE (both supplied by BASF, Ludwigshafen, W. Germany).

The coating dispersion containing the phosphor particles and the binder prepared as described above is applied uniformly onto the surface of the support to form a layer of the coating dispersion. The coating procedure may proceed according to any conventional method such as doctor blade coating, dip-coating or roll coating.

After applying the coating dispersion onto the support, the coating dispersion is then heated slowly to dryness so as to complete the formation of a phosphor layer.

An ultrasonic treatment can be applied to improve the packing density and to perform the de-aeration of the phosphor-binder combination.

The phosphor layer can be provided onto the support by the methods other than that given in the above. For instance, the phosphor is initially prepared on a sheet (false support) such as a glass plate, metal plate or plastic sheet using the aforementioned coating dispersion and then thus prepared phosphor layer is superposed on the genuine support by pressing or using an adhesive agent. Or, the phosphor layer may be applied to the support by employing a method such as vapor deposition, sputtering, spraying, etc.

In the preparation of a radiographic screen, one or more additional layers are occasionally provided between the support and the phosphor layer, so as to enhance the bonding between the support and the phosphor layer, or to improve the sensitivity of the screen or the quality of an image provided thereby. For instance, a subbing layer or an adhesive layer may be provided by coating polymer material such as gelatin over the surface of the support on the phosphor layer side. Otherwise, a light-reflecting layer or a light-absorbing layer may be provided by forming a polymer material layer containing a light-reflecting material such as titanium dioxide or a light-absorbing material such as carbon black. Such a layer may be coated on the support either as a backing layer or interposed between the support and the active layer. One or more of these additional layers may be provided on the support.

On the surface of the (stimulable) phosphor layer not facing the support, the radiation cured protective overcoat is provided.

Said protective overcoat is formed by a process in which a coating liquid containing at least one of a radiation curing type resin is applied onto the face of the (stimulable) phosphor layer and is subjected to irradiation by ultraviolet rays or electron beam to carry out curing of the coating liquid.

The monomers and prepolymers are selected in order to provide a crosslinking reaction for forming a solvent insoluble layer having good abrasion resistance.

Preferably, the radiation curing type resin is an urethaneacrylate, and more preferably an aliphatic urethaneacrylate. Radiation cured coating based on urethaneacrylates are known for their abrasion resistance.

To the polymer which is the abovementioned radiation curing type resin, there may be added, if necessary, a vinylmonomer as a reactive diluent, a non-reactive binder, a crosslinking agent, a photoinitiator, a photosensitizer, a storage stabilizer, a colorant, and other additives, and then dispersed therein to prepare the coating liquid for the protective layer. Examples of colorants that can be used in the protective layer include MAKROLEX ROT EG, MAKROLEX ROT GS and MAKROLEX ROT E2G, all three supplied by Bayer, Leverkusen, W. Germany.

A difunctional acrylate e.g. hexane diol diacrylate is preferably added as reactive diluent in an amount of between 0 and 50 % by weight, preferably between 10 and 30 % by weight. Higher functional acrylates would yield hard and brittle layers.

Curing by means of electron beam is particularly preferred in radiographic screen applications. The photoinitiator which needs to be added to the coating solution when using ultraviolet radiation as curing source will to a more or less extent also absorb the light emitted by the phosphor thereby impairing the sensitivity of the radiographic screen. This is particularly the case when a phosphor emitting UV or blue light is used; EB curing is then particularly preferred. In case of use of a green emitting phosphor a photoinitiator has to be chosen of which the absorption range overlaps to a minimum degree with the emission range of the phosphor; a preferred photoinitiator is then 2-hydroxy-2-methyl-l-phenyl-propan-l-one (DAROCUR 1173 supplied by E. Merck, Darmstadt, W. Germany).

The amount of the photoinitiator used is preferably within the range of 0.01 to 5 parts by weight relative to 100 parts by weight of the prepolymer. In particular, the photoinitiator is preferably used in an amount of 0.5 to 3 parts by weight and within the range of 3 to 7 times the amount of the radical-generating compound used.

A variety of other optional materials can be included in said surface coating of the radiographic screen, such as materials to reduce static electrical charge accumulation, plasticizers, matting agents, lubricants, defoamers and the like.

Examples of lubricants to be added include silicones such as SURFACTANT 190 supplied by Dow Corning Corporation, Midland, Michigan, USA, fluorine containing compounds such as polytetrafluoroethylene and LANCO WAX supplied by Georg M. Langer & Co., Bremen, W. Germany, waxes such as ACRAWAX supplied by Glyco Products, New York, USA and LANCO GLIDD supplied by Georg M. Langer & Co., Bremen, W. Germany. The lubricants are added in amounts varying between 0.01 and 0.5 % by weight.

Examples of defoamers to be added include LANCO ANTIBUBBLE L and LANCO FOAMSTOP PL both supplied by Georg M. Langer & Co., Bremen, W. Germany.

Although antistatics are more commonly included in the radiographic element which comes into contact with the radiographic screen small amounts of conventional antistatics may be added to the topcoat or to the active layer. Especially for the conventional X-ray conversion screens static electricity is usually built up during the exchange of the film into and out of the area or cassette containing the X-ray screens. This has been known to cause static marks by exposure of the sensitive photographic film. This cannot be tolerated.

Particularly preferred antistatics for incorporation in the phosphor layer or in the said radiation cured protective overcoat, as also for incorporation in other types of protective coatings formed of an organic film-forming polymer such as cellulose nitrate, cellulose acetate, polymethyl methacrylate and the like, are polyethylene oxides, preferably corresponding to the formula $RO\text{-}(CH_2CH_2O)_n\text{-}H$ with $n = 2$ and $R =$ cetyl or stearyl or oleyl. These compounds are added in an amount of 0-10 % by weight, preferably 2-4 % by weight. Using these compounds in combination with anionic or cationic antistatics (e.g. quaternary ammonium salts) leads to a synergetic effect.

The thickness of the protective layer formed according to the abovementioned process may be within the range of from 1 to 100 um, more preferably from 2 to 20 um.

To form the protective layer, the composition is coated at a suitable wet thickness (preferably between 60 and 100 um) and cured by subjecting it to radiation which converts it to a solid form. Any suitable method for coating a thin uniform layer of the composition can be employed. Examples of suitable coating methods include dip coating, air-knife coating, roll coating, extrusion coating, bead coating, curtain coating, and so forth.

Radiographic screens as described above can also be in the form of gradual screens, i.e. screens having a gradually or imagewise varying intensification along their length and/or width. This can be achieved by graduality in the thickness of the phosphor layer or by graduality in the amount of dye capable of absorbing the light emitted by the phosphor, into the protective layer.

The following examples are incorporated to illustrate the invention without however limiting it thereto.

## EXAMPLE 1 : Determination of surface free energies

A radiographic screen provided with a radiation cured coating (A) was prepared as follows.

Green emitting gadolinium oxysulfide phosphor (80 % by weight) was predispersed in a low viscous presolution (20 % by weight) of low binder content, together with a dispersant, by stirring for 5 minutes at 1700 rpm. The presolution consisted of 7 % by weight of polyethyl acrylate binder (PLEXISOL B 372 supplied by Röhm GmbH, Darmstadt, W. Germany), 18 % by weight of ethylacetate, 50 % by weight of methyl ethyl ketone, 25 % by weight of methylglycol and 0.5 % of GAFAC RM 610 (supplied by GAF, New York, USA). Subsequently, the residual amount of polyethyl acrylate binder and ethylacetate solvent was added to the phosphor predispersion to attain a solution with a solid content of 70 %, with 89 % by weight of phosphor against 11 % of binder.

The obtained phosphor dispersion was applied to a black colored subbed polyethylene terepthalate support by doctor blade coating (wet thickness 900 um). After evaporation of the solvent a phosphor layer of 160 um thickness was obtained.

A radiation curable coating was prepared comprising 80 % by weight of a mixture of 80 % of an aromatic urethaneacrylate (EBC 220 supplied by UCB, Drogenbos, Belgium) and 20 % of an aliphatic urethaneacrylate (EBC 264 supplied by UCB, Drogenbos, Belgium), 15 % by weight of hexane diol diacrylate, 4.5 % by weight of photoinitiator (DAROCUR 1173 supplied by E. Merck, Darmstadt, W. Germany) and 0.5 % by weight of a silicone surfactant. To this composition was added ethanol as solvent in an amcunt so as to obtain a 25 wt % solution.

The composition was applied onto the phosphor layer by dip coating (wet thickness about 100 um). After evaporation of the solvent a topcoat layer having a thickness of 10-15 um was obtained.

The coating was cured by UV radiation using a Labcure Unit supplied by Technigraf GmbH, Grävenwiesbach, W. Germany ($O_3$ removal, air cooling, energy output of 80 W/cm, velocity 5 m/min, distance UV source-substrate 11 cm).

The radiographic screen as such, i.e. the untreated radiographic screen is referred to below as (I).

A similarly prepared radiographic screen was treated with a composition comprising a saturated solution of barium hydroxide in water (50 % by volume), isopropanol (20 % by volume) and methanol (30 % by volume) as follows. A wad of cotton was soaked with the treating composition and subsequently the radiation cured coating was rubbed once with said wad. The interaction time was 5 minutes in wet state and 12 hours in dry state. The thus obtained treated radiographic screen is referred to below as (II).

A radiographic screen similar to screen (I) was treated with a composition comprising ureum 5 % in water as follows. The screen was dipped in the treating composition for 15 minutes at 50°C and subsequently rubbed dry. The interaction time was 12 hours in dry state. The thus obtained treated radiographic screen is referred to below as (III).

A radiographic screen similar to screen (I) was treated with a composition comprising ureum 5 % in water as follows. The screen was rubbed once with a wad of cotton soaked with the treating composition and subsequently dried. The interaction time was 12 hours in dry state. The thus obtained treated radiographic screen is referred to below as (IV).

A radiographic screen similar to screen (I) was treated with a composition comprising 25 ml of tetramethylammonium hydroxide 25 %, 25 ml water and 50 ml ethanol as follows. The screen was dipped in the treating composition for 5 minutes and subsequently dried and washed with water. The interaction time was 12 hours in dry state. The thus obtained treated radiographic screen is referred to below as (V).

A radiographic screen similar to screen (I) was treated with a composition comprising a saturated solution of barium hydroxide in water (50 % by volume), isopropanol (20 % by volume) and methanol (30 % by volume) as follows. A wad of cotton was soaked with the treating composition and subsequently the radiation cured coating was rubbed once with said wad. The interaction time was 5 minutes in wet state and 1 minute in dry state. The thus obtained treated radiographic screen is referred to below as (VI).

The surface free energy of each of the abovementioned screens (I) to (VI) provided with radiation cured coatings was determined by measuring the contact angle between the surface of the radiation cured coating and a series of well-characterized liquids. The contact angle was obtained by drawing a tangent to the enlarged profile of a drop of each liquid resting on the surface.

The obtained contact angles in ° for each of the treated coatings and the reference liquids are listed below in table 1.

Table 1

| screen<br>liquid | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| water | 63.0 | 62.1 | 61.0 | 54.0 | 68.9 | 42.3 |
| glycerine | 69.1 | 58.6 | 61.2 | 58.0 | 50.3 | 62.9 |
| formamide | 52.5 | 39.4 | 56.5 | 53.2 | 39.7 | 36.3 |
| methylene iodide | 48.6 | 37.7 | 47.4 | 50.3 | 35.8 | 47.5 |
| tricresyl phosphate | 43.7 | 33.4 | 42.3 | 41.1 | 29.0 | 40.7 |
| hexadecane | 24.6 | | | 22.7 | | |

The obtained surface free energy in mN/m of each of the radiation cured coatings ( $_s$) and its disperse (

$^{d}_{s}$) and polar ($^{p}_{s}$) components, as calculated from the measured contact angles listed in table 1 above and the values of $^{d}_{l}$ and $^{p}_{l}$ of the reference liquids in mN/m as listed below, are listed in table 2.

The contact angles obtained for water and formamide were not used to calculate the surface free energy of the coating.

| reference liquid | $^{d}_{l}$ | $^{p}_{l}$ |
|---|---|---|
| water | 18.7 | 53.8 |
| glycerine | 28.3 | 36.9 |
| formamide | 39.4 | 19.6 |
| methylene iodide | 49.5 | 1.3 |
| tricresyl phosphate | 32.0 | 8.9 |
| hexadecane | 27 | 0 |

Table 2

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| $_{s}$ | 35 | 47 | 38 | 38 | 45 | 37 |
| $^{d}_{s}$ | 26 | 33 | 31 | 26 | 36 | 26 |
| $^{p}_{s}$ | 9 | 14 | 6 | 11 | 9 | 11 |

By way of comparison: $_{s}$ of a non radiation cured protective coating of a radiographic screen (i.e., a cellulose acetobutyrate layer) is 42 mN/m, $^{d}_{s}$ = 29 mN/m and $^{p}_{s}$ = 12 mN/m. There are no problems regarding adherence to said layers.

Immersing the non treated coating (I) in water leads to breaking up into separate drops of water. As contrasted herewith, immersing the above treated coatings (II) to (VI) in water leads to spreading and the formation of a homogeneous water film on the surface, this being an indication of the fact that the surface free energy of the coating is increased as compared to (I).

EXAMPLE 2 : Correlation with the peel test

On each of the abovementioned coatings (I) to (VI) a thin layer (ca. 10 um) of a polymethyl methacrylate lacquer (comprising 10 g of DEGALAN 62/03 supplied by Degussa AG, Frankfurt, W. Germany, 40 g methyl ethyl ketone, 40 g toluene, 20 g butyl acetate and 0.15 g surfactant) or a nitrocellulose lacquer (comprising 10 g WALSRODER NITROCELLULOSE E510, supplied by Wolff Walsrode AG, Walsrode, W. Germany, 20 g ethylacetate, 40 g toluene, 40 g butylacetate and 0.15 g surfactant) was applied by spraying. After drying a piece of tape (Tesatape type 4101, supplied by Beiersdorf AG, Hamburg, W. Germany) was applied firmly to said layer and subsequently ripped off.

The adherence of the lacquer onto the radiation cured coating was checked visually by comparing treated and non-treated coatings on the tearing off of the lacquer coating together with the tape.

No improvement in adherence as compared to non treated coating is referred to as - (direct, easy peel off of the whole lacquer coating under the tape); strong improvement is referred to as + + + (no peel off of the lacquer coating under the tape).

Table 3

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| peel test | - | +++ | + | ± | +++ | + |

EXAMPLE 3 : Correlation with printability

The manufacturing number was thermal press printed on each of the abovementioned coatings (II) and (V) using black ink type Colarit VL912 or Codierfolie CO512 (both supplied by Leonard Kurz GmbH & Co., Fürth, W. Germany) in a printing machine type GEBA IP supplied by Gebr. Baier KG, Schlechtbach, W. Germany, or Pressar P16 supplied by MADAG Maschinen und Apparatebau Dietikon AG, Dietikon, Switzerland. The parameters were set as follows: temperature 150° C, pressure 300 kg, time 0.35 sec.

The ink adhered sufficiently to the coating. Supplementary a coating of polymethyl methacrylate lacquer (DEGALAN as described in example 2) may be applied so as to protect the ink from the screen cleaning agent that may be used subsequently.

EXAMPLE 4 : Influence of the pH

A radiographic screen provided with a radiation cured coating (B) was prepared as in example 1 except for the fact that no silicone surfactant was added to the radiation cured coating.

Several identical screens were treated with different compositions by rubbing the surface a number of times (n). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). The improvement in adherence was tested by the peel test as described above in example 2.

Table 4

| composition | pH | n | wet | dry | adherence |
|---|---|---|---|---|---|
| KOH 0.1 N<br>15% $C_7F_{15}COONH_4$ | 13 | 5 | 5 min | 1 min | +++ |
| $Ba(OH)_2/H_2O$/sat.<br>15% $C_7F_{15}COONH_4$ | 12-13 | 2 | 3 min | 1 min | +++ |
| $(CH_3)_4NOH$ 25%<br>25% $H_2O$/50% ethanol | 11-12 | 1 | 5 min | 1 min | +++ |
| $Ca(OH)_2/H_2O$ sat. | 10-11 | 30 | 5 min | 10 min | ++ |
| $Mg(OH)_2/H_2O$ sat. | 9-10 | 30 | 5 min | 12 h | ++ |
| $NEt_3$ 5 ml/$H_2O$ 20 ml<br>isopropanol 10 ml | 9-10 | 2 | 5 min | 1 min | ++ |
| ureum 5% / $H_2O$<br>15% $C_7F_{15}COONH_4$ | 7-8 | 1 | 5 min | 1 min | + |
| $H_2O$ | 7 | 1 | 1 min | 1 min | - |

The above results show that the improvement in adherence is greater when treating in similar circumstances with compositions having a higher pH.

EXAMPLE 5 : Influence of the spreading capacity of the treating composition

Several screens identical with the one described in example 4 were treated with different compositions by rubbing the surface a number of times (n) or by dipping the coating in the composition for some time at some temperature (*). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). The improvement in adherence was tested by the peel test as described above in example 2.

Table 5

| composition | pH | n | wet | dry | adherence |
|---|---|---|---|---|---|
| $Ba(OH)_2/H_2O$ sat. | 12-13 | 1 | 5 min | 1 min | - |
| $Ba(OH)_2/H_2O$ sat. | 12-13 | 10 | 5 min | 1 min | +++ |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | 12-13 | 1 | 3 min | 1 min | ++ |
| $Ba(OH)_2/H_2O$ sat.<br>15% $C_7F_{15}COONH_4$ | 12-13 | 2 | 3 min | 1 min | +++ |
| $NH_4OH$ 10% / $H_2O$ | 10-11 | 1 | 1 min | 1 min | - |
| $NH_4OH$ 10% / $H_2O$ (*) | 10-11 | 20 min | 20 min | 1 min | +++ |
| ureum 5% / $H_2O$ | 7-8 | 40 | 5 min | 1 min | ± |
| ureum 5% / $H_2O$<br>15% $C_7F_{15}COONH_4$ | 7-8 | 1 | 5 min | 1 min | + |
| ureum 5% / $H_2O$<br>50% isopropanol | 7-8 | 1 | 5 min | 1 min | + |
| ureum 5% / $H_2O$ (*) | 7-8 | 15 min<br>50°C | 15 min<br>50°C | 1 min | ++ |
| $H_2O$ | 7 | 1 | 1 min | 1 min | - |
| $H_2O$ (*) | 7 | 30 min<br>100°C | 30 min<br>100°C | 1 min | ++ |

The above results show that the improvement in adherence depends on the capability of the treating composition to spread on the surface of the coating, i.e. on the surface free energy of the composition itself. The spreading can be influenced (i.e. the surface free energy of the composition lowered) by adding surfactants such as $C_7F_{15}COONH_4$ or alcohols such as isopropanol and methanol. The spreading can also be influenced artificially by dipping the coating in the composition or by wetting several times.

EXAMPLE 6 : Influence of the interaction time

Several screens identical with either the screen as described in example 1 provided with the radiation cured coating (A) or with the screen as described in example 4 provided with radiation cured coating (B) were treated with different compositions by rubbing the surface a number of times (n). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). The improvement in adherence was tested by the peel test as described above in example 2.

Table 6

| composition | coating | pH | n | wet | dry | adherence |
|---|---|---|---|---|---|---|
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | B | 12-13 | 1 | 3 min | 1 min | ++ |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | B | 12-13 | 1 | 3 min | 60 min | +++ |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | B | 12-13 | 1 | 3 min | 12 h | +++ |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | A | 12-13 | 1 | 5 min | 1 min | + |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | A | 12-13 | 1 | 5 min | 60 min | ++ |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | A | 12-13 | 1 | 5 min | 12 h | +++ |
| $Ba(OH)_2/H_2O$ sat.<br>15% $C_7F_{15}COONH_4$ | A | 12-13 | 5 | 4 min | 1 min | ++ |
| $Ba(OH)_2/H_2O$ sat.<br>15% $C_7F_{15}COONH_4$ | A | 12-13 | 5 | 4 min | 12 h | +++ |
| $Ca(OH)_2/H_2O$ sat. | B | 10-11 | 30 | 5 min | 10 min | ++ |
| $Ca(OH)_2/H_2O$ sat. | B | 10-11 | 30 | 5 min | 12 h | +++ |
| $Ca(OH)_2/H_2O$ sat. | A | 10-11 | 30 | 5 min | 10 min | - |
| $Ca(OH)_2/H_2O$ sat. | A | 10-11 | 30 | 5 min | 12 h | + |
| $Mg(OH)_2/H_2O$ sat. | B | 9-10 | 30 | 5 min | 10 min | ++ |
| $Mg(OH)_2/H_2O$ sat. | B | 9-10 | 30 | 5 min | 12 h | ++ |
| $Mg(OH)_2/H_2O$ sat. | A | 9-10 | 30 | 5 min | 10 min | - |
| $Mg(OH)_2/H_2O$ sat. | A | 9-10 | 30 | 5 min | 12 h | ± |

These results show that the interaction time in wet state as well as in dry state is an important factor. If a moderate improvement in adherence is obtained after a short period of interaction, the improvement in adherence is very well after a longer period of interaction.

The results obtained by dipping the coating in the composition as shown in table 5 also demonstrate the effect of the interaction time.

EXAMPLE 7 : Influence of the temperature

Several screens identical with the one described in example 4 were treated with different compositions by rubbing the surface a number of times (n) or by dipping the coating in the composition for some time at some temperature (*). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). The improvement in adherence was tested by the peel test as described above in example 2.

Table 7

| composition | pH | n | wet | dry | adherence |
|---|---|---|---|---|---|
| KOH 0.1 N | 13 | 40 | 10 min | 1 min | + |
| KOH 0.1 N (*) | 13 | 10 min<br>50°C | 10 min | 1 min | +++ |
| ureum 5% / $H_2O$ | 7-8 | 40 | 5 min | 1 min | - |
| ureum 5% / $H_2O$ (*) | 7-8 | 15 min<br>50°C | 15 min | 1 min | ++ |

The above results show that the improvement in adherence increases with increasing temperature.

EXAMPLE 8 : Influence of the radiation cured coating

Several radiation cured coatings as identified below were treated with different compositions by rubbing the surface a number of times (n) or by dipping the coating in the composition for some time at some temperature (*). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). In the cases (**) the surface is thereafter rinsed with water. The improvement in adherence ($A_{tr}$) was tested by the peel test as described above in example 2. By way of comparison the adherence to the non treated coating ($A_{ntr}$) is also shown.

Coating A represents the coating as described in example 1.

Coating B represents the coating as described in example 4.

Coating C represents the coating as used on the COPYPROOF packaging by Agfa-Gevaert N.V., Mortsel, Belgium.

Coating D represents an ink type UVN/70 of Entreprises Kurfürst, Brussels, Belgium.

Coating E represents an urethaneacrylate lacquer type B4655 supplied by Reliance Universal N.V., Mechelen, Belgium.

Coating F represents an epoxyacrylate lacquer type V27885-1 (overprint varnish) of Jänecke & Schneemann, Drukinkten Arets, Wilrijk, Belgium.

Coating G represents an epoxyacrylate in tripropyleneglycol diacrylate (EBC 605 supplied by UCB, Drogenbos, Belgium).

Coating H represents an epoxyacrylate in hexanediol diacrylate (EBC 604 supplied by UCB, Drogenbos, Belgium).

Coating I represents a lacquer type formulated by UCB, Drogenbos, Belgium for Velpa, Anderlecht, Belgium for use as paper overprint varnish consisting of 19 parts epoxyacrylate EBC 605, 19 parts urethaneacrylate EBC 210, 35 parts tripropylene glycol diacrylate, 14 parts hexanediol diacrylate, 5 parts benzophenone, 8 parts of an unsaturated tertiary amine and a silicone slipping agent.

Coating J represents an EB cured protective coating for a radiographic screen as described in example 1 with the difference that a blue emitting yttrium tantalate phosphor was used instead of the gadolinium oxysulfide phosphor employed in example 1, comprising 80 % of a mixture of 20 % of an aromatic urethaneacrylate (EBC 220 supplied by UCB, Drogenbos, Belgium) and 80 % of an aliphatic urethaneacrylate (EBC 264 supplied by UCB, Drogenbos, Belgium) and 20 % of hexane diol diacrylate. The coating was cured by subjecting to electron beam radiation in an ESI Labcure unit at 4 megarad, 150 kV and inertisation 100 ppm oxygen.

Coating K represents an epoxide coating comprising 53.3 % of CYRACURE resin UVR-6100, 14.3 % of CYRACURE diluent UVR-6200, 27.9 % of CYRACURE flexibilizer UVR-6379, 4 % of CYRACURE fotoinitiator UVI-6990 (all supplied by Union Carbide Corporation, Danbury, USA) and 0.5 % of a flow control agent/surfactant that is UV cured ( 3 x 20 m/min, 80 W/cm).

Coating L represents a coating similar to coating K except for the fact that coating L is UV cured and afterwards thermally cured (to complete the curing) for 7 minutes at 130 ° C.

Table 8

| composition | coating | pH | n | wet | dry | $A_{tr}$ | $A_{ntr}$ |
|---|---|---|---|---|---|---|---|
| $Ba(OH)_2/H_2O$ sat. | B | 12-13 | 10 | 5 min | 1 min | +++ | - |
| $Ba(OH)_2/H_2O$ sat. | A | 12-13 | 40 | 4 min | 1 min | + | -- |
| $(CH_3)_4NOH$ 25% $H_2O$/ethanol | B (**) | 11-12 | 1 | 5 min | 3 min | +++ | - |
| $(CH_3)_4NOH$ 25% $H_2O$/ethanol | A (**) | 11-12 | 1 | 5 min | 3 min | +++ | -- |
| $Ca(OH)_2/H_2O$ sat. | B | 10-11 | 30 | 5 min | 10 min | ++ | - |
| $Ca(OH)_2/H_2O$ sat. | A | 10-11 | 30 | 5 min | 10 min | - | -- |
| $Ca(OH)_2/H_2O$ sat. | A | 10-11 | 30 | 5 min | 12 h | + | -- |
| $Mg(OH)_2/H_2O$ sat. | B | 9-10 | 30 | 5 min | 10 min | ++ | - |
| $Mg(OH)_2/H_2O$ sat. | A | 9-10 | 30 | 5 min | 10 min | - | -- |
| $Mg(OH)_2/H_2O$ sat. | A | 9-10 | 30 | 5 min | 12 h | + | -- |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $NEt_3$ 5 ml/$H_2O$ isopropanol 10 ml | B | 9-10 | 2 | 5 min | 1 min | ++ | - |
| $NEt_3$ 5 ml/$H_2O$ isopropanol 10 ml | A | 9-10 | 2 | 5 min | 1 min | + | -- |
| ureum 5% / $H_2O$ (*) | B | 7-8 | 15 min 50°C | 15 min 50°C | 1 min | ++ | - |
| ureum 5% / $H_2O$ (*) | B | 7-8 | 15 min 50°C | 15 min 50°C | 12 h | +++ | - |
| ureum 5% / $H_2O$ (*) | A | 7-8 | 15 min 50°C | 15 min 50°C | 12 h | + | -- |
| ureum 5% / $H_2O$ (*) | A | 7-8 | 15 min 50°C | 15 min 50°C | 1 min | - | -- |
| ureum 5% / $H_2O$ (*) | B | 7-8 | 30 | 5 min | 10 min | + | - |
| ureum 5% / $H_2O$ (*) | B | 7-8 | 30 | 5 min | 12 h | + | - |
| ureum 5% / $H_2O$ (*) | A | 7-8 | 30 | 5 min | 10 min | - | -- |
| ureum 5% / $H_2O$ (*) | A | 7-8 | 30 | 5 min | 12 h | - | -- |
| $H_2O$ | B | 7 | 30 min 100°C | 30 min 100°C | 1 min | ++ | - |
| $H_2O$ | A | 7 | 30 min 100°C | 30 min 100°C | 1 min | - | -- |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | C | 12-13 | 1 | 3 min | 1 min | +++ | - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | D | 12-13 | 1 | 3 min | 1 min | +++ | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | E | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | F | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | G | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | G | 12-13 | 15 min<br>100°C | 15 min<br>100°C | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | H | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | I | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>$C_7F_{15}COONH_4$ | J | 12-13 | 1 | 3 min | 1 min | +++ - |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | K | 12-13 | 2 | 2 min | 12 h | +++ + |
| $Ba(OH)_2/H_2O$ sat.<br>methanol/isopropanol | L | 12-13 | 2 | 2 min | 12 h | +++ + |
| $(CH_3)_4NOH$ 25%<br>$H_2O$/ethanol | K | 11-12 | 2 | 2 min | 2 min<br>120°C | +++ + |
| $(CH_3)_4NOH$ 25%<br>$H_2O$/ethanol | L | 11-12 | 2 | 2 min | 2 min<br>120°C | +++ + |

These results show that the method according to the present invention can be used on a wide variety of radiation cured coatings. Epoxide based radiation cured coatings (coatings K and L) represent less problems in adherence than acrylate based radiation cured coatings.

Coatings comprising silane compounds (coating A) are worse in adhering properties compared to coatings without said compound (coating B).

EXAMPLE 9 : Forming of the alkaline compound in situ

Several screens identical with the screen as described in example 4 provided with radiation cured coating (B) were treated with different compositions by rubbing the surface a number of times (n). The composition was allowed to interact with the surface of the coating for some time in wet state (wet) and in dry state (dry). In some cases the surface was thereafter wiped with water (**). The improvement in adherence was tested by the peel test as described above in example 2.

Table 9

| composition | n | wet | dry | adherence |
|---|---|---|---|---|
| $NaOCH_3$ 5% / methanol<br>isopropanol | 1 | 1 min | 2 h | - |
| $NaOCH_3$ 5% / methanol (**)<br>isopropanol | 1 | 1 min | 2 h | +++ |
| $NaOCH_3$ 5% / methanol<br>isopropanol | 1 | 1 min | 1 min | - |
| $NaOCH_3$ 5% / methanol<br>isopropanol / 10 ml $H_2O$ | 1 | 1 min | 1 min | + |
| $NaOCH_3$ 5% / methanol<br>isopropanol / 10 ml $H_2O$ | 1 | 1 min | 2 h | ++ |
| $Na_2SO_3$ 5% / $H_2O$ | 10 | 5 min | 10 min | ++ |

**In the cases (**) or in case of adding $H_2O$ to the treating composition the alkaline compound is formed in situ.**

EXAMPLE 10 : Adherence to another radiation cured coating

A radiation curable composition comprising 5 g of EBC 264 (supplied by UCB, Drogenbos, Belgium), 95 g of methyl ethyl ketone and 0.5 g of DAROCUR 1173 (supplied by E. Merck, Darmstadt, W. Germany) was sprayed on the radiation cured coating A or B treated with a saturated aqueous solution of $Ba(OH)_2$ containing isopropanol and methanol, and thereafter cured by UV irradiation.

The adherence of the radiation cured topcoat on the radiation cured coating was tested by the peel test as described above in example 2 and yielded as result + + +.

EXAMPLE 11 : Currently known pretreatment methods

Some currently known pretreatments for improving the adherence to plastics were tested on a UV cured urethaneacrylate coating.

Corona discharge treatment does not improve the adherence as shown by the peel test and the wetting by water.

Etching with diluted acids does not improve the adherence. Treating with a 10 % or 30 % aqueous

$H_2SO_4$ solution or a 10 % aqueous $HNO_3$ solution for 5 sec corrodes the coating; the coating discolores. Treating with a 10 % aqueous HCl or HT solution for 5 sec does not affect the coating at all.

## Claims

1. Method for improving the adherence to a radiation cured coating comprising treating the coating with a composition having a pH of at least 7 so that the surface free energy of the radiation cured coating increases to at least about 37 mN/m.

2. Method according to claim 1, characterized in that said treatment is such that the surface free energy increases to at least about 45 mN/m.

3. Method according to claim 1 or 2, characterized in that the radiation cured coating is based on multifunctional acrylates or on epoxides.

4. Method according to any one of the preceding claims, characterized in that the composition has a pH greater than 10.

5. Method according to any one of the preceding claims, characterized in that the composition comprises an alkali or earth alkali metal hydroxide or a quaternary ammonium hydroxide.

6. Method according to claim 5, characterized in that the composition comprises barium hydroxide or tetramethylammonium hydroxide.

7. Method according to any one of the preceding claims, characterized in that the composition comprises a spreading agent.

8. Method according to claim 7, characterized in that the spreading agent is a surfactant or an alcohol.

9. Method according to any one of the preceding claims, characterized in that the composition is applied by rubbing the surface of the radiation cured coating a few times with the composition or by dipping the radiation cured coating in the composition for some time.

10. Method according to any one of the preceding claims, characterized in that the radiation cured coating is a protective coating on a radiographic screen.

11. Method according to claim 10, characterized in that the radiographic screen is a conventional X-ray conversion screen or a stimulable X-ray conversion screen.

12. Method according to claim 10 or 11, characterized in that the radiation cured coating is based on urethaneacrylate.

13. Method according to any one of claims 10 to 12, characterized in that the radiation cured coating comprises a silicone surfactant in an amount of from 0.01 to 0.5 % by weight.

14. Method according to any one of claims 10 to 13, characterized in that the protective coating has been cured by electron beam radiation.

15. Method according to any one of claims 10 to 13, characterized in that the protective coating has been cured by ultraviolet radiation using 2-hydroxy-2-methyl-l-phenyl-propan-l-one as photoinitiator.

16. Radiographic screen comprising a radiation cured protective coating provided with printed information, characterized in that said protective coating has been treated according to the method of any of the preceding claims before or during printing, to improve the adherence of the printed information.

European
Patent Office

# EUROPEAN SEARCH REPORT

Application Number

**EP 91 20 0564**

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| A | EP-A-0 234 532 (DU PONT)<br>* page 5, line 1 - page 6, line 11; claims 1-10 *<br>- - - | 1,3,7-11,<br>13 | G 21 K 4/00 |
| A | EP-A-0 193 197 (DU PONT)<br>* claims 1-15 *<br>- - - | 1,3,10,11 | |
| A | EP-A-0 103 874 (DU PONT)<br>* claims 1-9 *<br>- - - | 1,3,10,11 | |
| A | DE-A-2 640 014 (SIEMENS)<br>* claims 1-4 *<br>- - - - - | 1,3,10,11 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | G 21 K |

The present search report has been drawn up for all claims

| Place of search | Date of completion of search | Examiner |
|---|---|---|
| The Hague | 12 June 91 | DROUOT M.C. |

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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