A water-based coating composition which may be air dried to form durable, fire resistant coatings includes dispersed vinylidene fluoride polymer particles, emulsified liquid epoxy resin and a dissolved emulsifying agent which is also capable of rapidly curing the epoxy resin upon removal of the water from the composition.
AQUEOUS VINYLDENE FLUORIDE POLYMER COATING COMPOSITION

The invention described herein was made in the performance of work under NASA Contract No. NAS 9 - 14403 and is subject to the provisions of section 305 of the National Aeronautics and Space Act of 1958 (72 Stat. 435; 42 U.S.C. 2457).

This invention relates to an air-drying latex, topcoat formulation including components which are compatible and relatively stable in a liquid composition. Resinous vinyldene fluoride polymer is present in the formulation as the film-former while a liquid epoxy resin and a water-soluble emulsifier for the epoxy resin, which is also a curing agent for the epoxy after removal of the water, provide additional beneficial coating properties.

Various systems have been devised for laying down films and protective coatings of normally solid, high molecular weight vinyldene fluoride polymers to give substrates the protection of polymeric coatings which have good solvent resistance, chemical resistance, weather resistance, heat stability, strength, and resilience. However, these known systems have certain disadvantages with regard to processing conditions and environmental contamination. For example, U.S. Pat. No. 3,169,120 describes vinyldene fluoride polymer particles dispersed in an aqueous composition containing a major proportion of at least one water miscible solvent selected from the group consisting of triethylphosphate, dimethyl succinate, diethyl succinate and tetraethylurea. The disadvantages of this system are the presence of large amounts of undesirable, high boiling point solvents and the necessity for drying and curing the polymer film at temperatures in excess of about 175° C. U.S. Pat. Nos. 3,324,069 and 3,340,222 deal with film-forming compositions comprised of vinyldene fluoride polymer and an acrylate polymer dispersed in a latent solvent for the vinyldene fluoride polymer, the latent solvent being a volatile organic liquid. The polymer films and coatings formed from such non-aqueous dispersions are dried and cured at temperatures on the order of 230° C. With the ever increasing emphasis being placed on environmental protection, the presence of large amounts of such volatile and toxic organic solvents in coating compositions is objectionable because of their air-polluting effects.

High quality vinyldene fluoride polymer films and coatings can be prepared from the non-polluting, substantially solvent-free, coating composition of this invention which coating composition permits drying and curing of the formed coatings at ambient temperature, i.e., about 15° to 50° C., although, if desired, the films and coatings may be quickly dried and cured at high temperature, i.e., up to about 290° C. The dried and cured coatings have superior hardness, abrasion resistance, adhesion properties, flexibility, resistance to chemicals, corrosion protection, weathering properties, thermal stability, fire resistance, and clarity.

Accordingly, this invention comprises an aqueous coating composition containing for each 100 parts by weight of aqueous liquid medium from about 25 to about 125, preferably about 30 to about 70, parts of dispersed vinyldene fluoride polymer particles and from about 3 to about 50, preferably about 8 to about 20, parts of emulsified liquid epoxy resin, and, for each part by weight of liquid epoxy resin, from about 0.25 to about 2.5, preferably about 1.0, parts of emulsifying agent for said epoxy resin which agent is capable of rapidly curing said epoxy resin on removal of water from said composition.

By the term "vinyldene fluoride polymer" used herein is meant not only the high molecular weight normally solid homopolymer resin of vinyldene fluoride but also the high molecular weight normally solid copolymers of vinyldene fluoride with at least one comonomer, for example, those selected from the group consisting of tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, hexafluoropropene and mixtures thereof, said copolymers consisting of at least about 50 mole % of polymerized vinyldene fluoride units. A particularly preferred copolymer (terpolymer) is that composed of about 62 weight percent vinyldene fluoride, about 24 weight percent of tetrafluoroethylene, and about 14 weight percent of hexafluoropropene. The vinyldene fluoride polymer is present in the dispersion embodied herein as dispersed particles having a particle size range of 0.1 micron or smaller up to about one micron.

Examples of the emulsifiable, liquid epoxy resins which are usually employed for the composition of this invention are set forth in U.S. Pat. No. 3,719,629. The patent discloses glycidyl ethers of polyhydric compounds which include, for example, glycidyl ethers of phenols, bisphenols, phenol-aldehyde condensation products, glycols, polyoxyalkylene glycols and the like, or mixtures of such glycidyl ethers. One preferred epoxy resin component for this invention is a blend of from about 10-12 parts by weight of a liquid epoxy resin of the diglycidyl ether of bisphenol A with from about 1-3 parts of a liquid epoxy resin of the diglycidyl ether of propylene glycol.

The emulsifying agent for the liquid epoxy resin which also acts as a curing agent for the epoxy resin when the composition is dried, is advantageously selected from aminomethylelated vinyl interpolymer of the type described in U.S. Pat. No. 3,634,372 wherein the aminomethylelated radical is acidified. The acidification of such copolymers to provide water thinnable coating composition with dispersed epoxy resin is also disclosed in the above mentioned U.S. Pat. No. 3,719,629, and the disclosure of both of the above patents are incorporated herein by reference. The aminomethylelated copolymers are further characterized as having pendant aminomethylelated groups of the formula

$$\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{CH(CH2)NHR1R2} \\
\text{H}
\end{array}
\]
$$

where R1 and R2 are independently hydrogen or lower alkyl radicals, and n ranges from about 1.0 to 2.5. The intermediate vinyl carboxylic acid interpolymer are prepared, for example, by copolymerizing a vinyl carboxylic acid, e.g., acrylic, methacrylic, cinnamic, crotonic acid and the like, with one or more copolymerizable monomers such as vinyl aromatic and aliphatic monomers. Preferable vinyl aromatic monomers are styrene, α-methylstyrene, and vinyl toluene. Preferable vinyl aliphatic monomers are methyl, ethyl, isopropyl, butyl and 2-ethylhexyl acrylates or methacylates. The vinyl interpolymer are preferably prepared with a sufficient amount of vinyl carboxylic acid monomer to provide at least 3 percent and preferably from about 7.5 to about 12 percent by weight of carboxylic acid (as
—COOH) and the balance of said interpolymer composed of the preferred comonomers as indicated above.

The aminooxyalkylated interpolymer employed in this invention are prepared by an amination reaction in which the vinyl carboxylic acid interpolymer in a suitable solvent is reacted with an excess (at least two moles) of alkyleneimine or N(aminoalky1)-substituted alkyleneimine. Suitable alkyleneimines include ethyleneimine, propyleneimine, butyleneimine and the like and mixtures thereof. Particularly useful N(aminoalky1)-substituted alkyleneimines are N-(2-aminoethyl)aziridine, N-(3-aminopropyl) aziridine, N-(2-aminopropyl)-propyleneimine and the like.

The acidification of the aminooxyalkylated vinyl polymer can be accomplished by the simple mixing of the polymer and acid in a suitable water miscible solvent or solvent blend using, as the acid, one which will form an acid salt with the pendant amine moieties. For example, suitable acids include hydrochloric acid, phosphoric acid, formic and acetic acid. The emulsifying agent is advantageously employed to formulate coating composition as a suspension in an inert liquid carrier, preferably water or a mixture of water and a water miscible solvent.

Coating composition additives may be, and preferably are, used for the composition of this invention. Dispersed, finely-divided pigments to give the coating or film the desired opacity, color or aesthetic appeal are used in amounts ranging from about 10 to about 170 parts by weight of pigment for each 100 parts by weight of vinylidene fluoride polymer resin with the provision, however, that total solids in the dispersion is not greater than about 200 parts per 100 parts by weight of water. Representative pigments are rutile titanium dioxide, various silicates such as talc, mica and clays, barytes, carbon black, zinc oxide, zinc sulfide, silicas, iron oxides, chrome oxides, and others may also be included in the composition. The preferred pH for the composition of this invention is in the range of about 5 to about 6.

The coating compositions can be applied to a wide variety of substrates including wood, metals, plastic, textiles, fabrics, paper, glass, etc. by conventional coating methods such as spraying, brushing, dipping, casting, knife coating, coil coating, reverse roll coating and other methods known in the art. The unexpected advantages of the aqueous dispersion of this invention derive from the discovery that durable, hard, and tough coatings are obtained by air-drying at ambient temperatures, i.e., 15° to 50° C. Accordingly, the coatings may be applied as high performance maintenance paints in plants and other commercial facilities to protect wood and metal surfaces.

Although adhesion of the film of the polymeric mixture to substrates is generally more than adequate, increased adhesion is obtained by first priming the substrates with a compatible coating layer. For example, for wood, a useful primer is a layer of pigmented acrylic acid ester polymer described in U.S. Pat. No. 3,234,039 and in U.S. Pat. No. 3,037,881. For metal coatings, a preferred primer layer is described in U.S. Pat. No. 3,111,426, that is an epoxy-based primer. Acrylic based primers are also useful for metals, as described in U.S. Pat. No. 3,526,532. For coatings on glass cloth or other flexible substrates, woven or non-woven, known adhesion promoters may be used. In particular, glass fiber may be first treated with a silane coupling agent as described by I. L. Fan & R. G. Shaw, Rubber World, June 1971, page 56. Air-drying of the aqueous base polymer coatings on substrates such as paper, glass fiber, glass cloth, and non-woven textiles may be accomplished at ambient temperatures with drying periods of about 3 to 24 hours. However, with forced air-drying at about 50° C the coatings will dry in 10 to 15 minutes. At 60° C about 5 to 10 minutes are adequate using forced air-drying. In all cases, coatings of the polymers mixture are smooth, glossy, and uniform, and the films adhere tenaciously to the substrate.

The following example is set forth to further demonstrate this invention.

**EXAMPLE**

A paint composition was prepared from a three component system as follows:

<table>
<thead>
<tr>
<th>PART A</th>
<th></th>
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<tbody>
<tr>
<td>Aminoethylated hydrochloride salt of acrylic copolymer (XCD 7080)**</td>
<td>50 grams (g.)</td>
</tr>
<tr>
<td>Pigment (finely-divided TiO₂)</td>
<td>100 g.</td>
</tr>
<tr>
<td>Defoamer (DAPRO DF 911)</td>
<td>0.6 g.</td>
</tr>
<tr>
<td>Cyclclohexanone</td>
<td>8.0 g.</td>
</tr>
<tr>
<td>Dianized water*</td>
<td>75. g.</td>
</tr>
</tbody>
</table>

**PART B**

Liquid epoxy resin of diglycidyl ether of bisphenol A (DER 331)** | 18.5 g. |
Liquid epoxy resin of diglycidyl ether of propylene glycol (DER 702)** | 3.4 g. |
Methyl Cellosolve Acetate | 6.1 g. |

The above components of Part B are mixed together to obtain a homogeneous mixture.

**PART C**

Latic of resinous terpolymer of 62 wt. % vinylidene fluoride 34 wt. % tetrafluoroethylene and 14 wt. % hexafluoropropene (32.4% resin in aqueous medium) | 192.9 g. |

*Water is added with low shear mixing after dispersing other components at high shear.
**Products of Dow Chemical Co.

Part B is added to Part A with gentle stirring. When a homogeneous mixture is obtained, Part C is added in a similar fashion. The resulting paint has an epoxy resin-curing agent content of about 31.5% of total resin solids in the composition and is shelf stable for up to six days at room temperature. It can be applied by brush, roller, or spray to metals such as aluminum, steel, and titanium, and to wood. The coating dries to the touch in about one hour under ordinary ambient temperature and humidity conditions and is fully cured after 24 hours. The cured coatings show hardness, adhesion, abrasion resis-
tance, flexibility, resistance to chemicals, and thermal stability as good or better than those of commercial
cobbyester-based polyurethane or polyester coatings. Ex-
cellent corrosion protection is obtained when the coat-
ing is applied over a conventional primer containing
rust inhibitors, e.g., acrylic or epoxy primer either latex
or solvent-based. In addition, the coating has excellent
weathering properties as determined by accelerated
tests and is self-extinguishing when applied to non-
flammable substrates.

Similar coating preparations employing other vinyl-
dene fluoride polymer resins and other liquid epoxy
resins or combinations thereof are prepared in a like
manner and display excellent modified coating proper-
ties.

The coating compositions of this invention are unique
in that they are easily prepared compatible composi-
tions which provide improved coating properties.

We claim:

1. An aqueous coating composition comprising, for
each 100 parts by weight of aqueous liquid medium,
from about 25 to about 125 parts of dispersed polymer
particles of vinylidene fluoride homopolymer or co-
polymer of at least 50 mol percent vinylidene fluoride
copolymerized with at least one other copolymerizable
monomer and from about 3 to about 50 parts of emulsi-
ﬁed liquid epoxy resin, and, for each part by weight of
liquid epoxy resin, from about 0.25 to about 2.5 parts of
an emulsifying agent comprising an acidified aminoalk-
ylated polymer having pendant aminooalkylate groups of
the formula

wherein R₁ and R₂ are independently selected from the
GROUP consisting of hydrogen and lower alkyl radicals
having 1 to 4 carbon atoms and the average value of n
ranges from about 1.0 to 2.5, and wherein said amin-
oalkylated polymer before aminoalkylation contains at
least 3% by weight pendant-COOH groups.

2. The composition of claim 1 wherein the vinylidene
fluoride polymer is a copolymer of about 62 weight
percent vinylidene ﬂuoride, about 24 weight percent
tetrafluoroethylene and about 14 weight percent of
hexafluoropropane.

3. The composition of claim 1 wherein the liquid
epoxy resin consists of a mixture of from about 10 to
about 12 parts by weight of a liquid epoxy resin of the
diglycidyl ether of bisphenol A and from about 1 to
about 3 parts by weight of a liquid epoxy resin of the
diglycidyl ether of propylene glycol.

4. The composition of claim 1 which contains from
about 10 to about 170 parts by weight of dispersed,
ﬁnely-divided pigment for each 100 parts by weight of
vinylidene ﬂuoride polymer.

5. The composition of claim 2 wherein the liquid
epoxy resin consists of a mixture of from about 10 to
about 12 parts by weight of a liquid epoxy resin of the
diglycidyl ether of bisphenol A and from about 1 to
about 3 parts by weight of a liquid epoxy resin of the
diglycidyl ether of propylene glycol.

6. The composition of claim 5 which contains from
about 10 to about 170 parts by weight of dispersed,
ﬁnely-divided pigment for each 100 parts by weight of
vinylidene ﬂuoride polymer.