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MASTER

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Attention: Dr. John R. Rossmeissl

Gentlemen:

Subject: UV Radiation Curable Paints, Contract DE AC01-79CS40210
Topical Report on Material Identification

The Westinghouse approach to the problem of finding alternatives to natural gas in product finishing is to develop ultraviolet radiation curable paints for application on preformed structures. The starting point of this program was the matching of resins, photoinitiators and pigments which will result in coatings that can be cured by ultraviolet radiation. The end point will be the application of these coatings to prefabricated metal structures to demonstrate the viability of this technique in producing commercially acceptable painted products. These UV curable paints should produce films that are hard, adherent and opaque at a nominal thickness of one mil (0.001 inch).

The desired physical characteristics are: pencil hardness of at least 2H, 100% adhesion as tested by the crosshatch method, complete hiding power and a low viscosity (60 centipoises) for ease of spray application.

In a normal paint development, the resin binder is chosen first, then suitable pigments are added followed by various modifiers such as extenders and flow control agents.

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In the development of UV curable paints, the procedure is reversed owing to the inter-relationship of those components, the absorption spectra of the photoinitiators and the UV radiation source output spectra. During the course of this program experimental data confirmed that these photo-active components, unlike most traditional paint materials, exhibit a high degree of interaction with other components in the coating system and thus require testing in combination. Furthermore, since the program is on the leading edge of this technology, new photoreactive materials which may be useful are constantly being developed. Consequently, Task I of this program, The Identification of Materials, will not be concluded until complete final paint formulations are achieved.

The initial work in this program was the identification of reactive diluents and base resins that are sensitive to the UV curing process. The reactive monomeric diluents tested included multifunctional acrylates, monofunctional acrylates and non-acrylic unsaturated esters. The multifunctional acrylates which showed high reactivity when photoinitiated using isopropyl benzoin ether (Stauffer Chemical Co., Vicure V-10) are listed below:

pentaerythritol tetraacrylate (PETA)
pentaerythritol triacrylate (PETriA)
trimethylolpropane triacrylate (TMPTA)
tetraethyleneglycol diacrylate (TEGDA)
diethyleneglycol diacrylate (DEGDA)
hexanediol diacrylate (HDDA)
triethylene glycol dimethacrylate (TEGDMA)
1,3-butylene dimethacrylate (BDMA)

Because of its high reactivity, HDDA was chosen as a diluent to reduce viscosity when added to base resins. The simple acrylates, methoxyethyl acrylate (MEA), 2-ethoxyethyl acrylate (EEA), butoxyethyl acrylate (BEA) showed only a moderate degree of reactivity when photoinitiated using Vicure V-10. However, when EEA was added to the base resin and photoinitiated using V-10, it gave films with increased flexibility. On the other hand, the non-acrylic ester monomers were generally unreactive when photoinitiated using V-10, although acrylic acid and methacrylic acid formed polymeric gels which precipitated.

The viscosity and cure time of several systems, which combined various resins and reactive diluents, were determined, and the properties of their films were evaluated by conical mandrel bend, impact, abrasion and hardness tests. In a system photoinitiated using V-10 accelerated with n-methyldiethanol amine (MDEA) and di-tertiarybutyl perbenzoate (DTBP), the most promising resin was the Hughson Chemical Co. acrylated urethane TS-3577-11, diluted with HDDA and EEA.

At this point in the program, it became increasingly clear that the photochemical effects were complicated by the ability of certain photosensitive systems to also act as thermal initiators, as for example, systems containing benzoyl peroxide or DTBP. This led to further study of UV lamp output spectra which should coincide with the absorption spectra of pigmented coating systems.

An important criterion in the choice of pigments in their effect on UV light penetration of films. It is well known that titanium dioxide (TiO_2) is used universally by the paint industry because it provides superior hiding power at lower pigment volume concentration and film thickness. Due to screening and competition with other UV absorbers in a system, TiO_2 can hinder cure. On the other hand, the light scattering ability of TiO_2 can also enhance cure.

The most promising photoinitiators, 2-chlorothioxanthone (CTX), benzil, 2-ethylanthraquinone (EAQ) and 2-methylanthraquinone (MEAQ), all absorb in the UV spectral range which is not screened by TiO_2. Coinitiators such as tertiary amines, aryl chloromethyl and chlorosulfonyl compounds and other photoinitiators were investigated in formulations also containing CTX, benzil, EAQ and MEAQ. The following compounds exhibited coreactivity:

n-methyldiethanolamine (MDEOA)
diethylenetriamine (DETA)
monethanolamine (MEOA)
diethanolamine (DEOA)
triethanolamine (TEOA)
n-n-dimethylaminoethylmethacrylate (DMAEMA)
phenethylamine (PEA)
triethylamine (TEA)
dimethylethanolamine (DMEOA)
morpholine (MORPH)
ethyl para-dimethylaminobenzoate (EPDMAB)
quinoline sulfonyl chloride (QSC)
Virginia Chemical Co. Uvecryl P101
Virginia Chemical Co. Uvecryl P102
Virginia Chemical Co. Uvecryl P104
Stauffer Chemical Co. Vicure 30
(benzoin isobutylether, V-30)
Michler's Ketone (4,4 bis(n,n-dimethyl amino) benzophenone)

Combinations of CTX with MDEOA and of benzil with morpholine were among the candidate coinitiators chosen for further modification.

Paints containing all of the aforementioned photoreactive agents cured by free radical polymerization (Appendix I). A cationic mechanism may also be used for curing paints by ultraviolet radiation (Appendix II). A system polymerizable by cationic initiation usually consists of: a base resin, reactive diluents, pigments, photoinitiators and photosensitizers. Union Carbide ERL 4221 was chosen as the base resin owing to its ability to form hard adherent films. The use of butyl glycidyl ether, n-butanol, and limonene dioxide as reactive diluents did not improve film flexibility. The most common cationic photoinitiators are the so-called "onium" salts. The 3M Co. FC-509 was most suited for pigmented coatings because of its absorption spectrum. Since the sulfonium and iodonium salts cannot be activated directly by UV radiation in a pigmented coating, a photosensitizer for energy transfer must be used. Photosensitizers which are suitable for use in pigmented coatings are 3M Co. FC-510, CTX and TX.

Further work to optimize these coating systems will continue as will the continuing evaluation of new materials until the final formulation is completed.

Very truly yours,

Carl P. Izzo

Carl P. Izzo
Program Manager

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Att.

APPENDIX I

FREE RADICAL POLYMERIZATION PHOTOINITIATION MECHANISMS

INITIATOR RADICAL FORMATION

$A \xrightarrow{h\nu} {}^1A^*$	absorption
${}^1A^* \longrightarrow A$	singlet decay
${}^1A^* \longrightarrow {}^3A^*$	intersystem crossing
${}^3A^* \longrightarrow B\cdot + C\cdot$	radical formation
${}^3A^* + R\text{-}H \longrightarrow AH\cdot + R\cdot$	H - transfer
${}^3A^* + R\text{-}H \longrightarrow {}^3[A{-}{-}{-}HR]^*$	triplet complex formation
${}^3[A{-}{-}{-}HR]^* \longrightarrow AH\cdot + R\cdot$	H - transfer
${}^3[A{-}{-}{-}HR]^* \longrightarrow A^{\cdot -} + RH^{\cdot +}$	electron-transfer
$A^{\cdot -} + RH^{\cdot +} \longrightarrow AH\cdot + R\cdot$	H - transfer
$AH\cdot + R\cdot \longrightarrow A + RH$	quenching
${}^3[A{-}{-}{-}{-}HR]^* \longrightarrow A + RH$	quenching
${}^3A^* + RX \longrightarrow A + {}^3RX^*$	energy transfer
${}^3RX^* \longrightarrow R\cdot + X\cdot$	cleavage and radical formation
${}^3RX^* \longrightarrow RX$	quenching
${}^3A^* + Q \longrightarrow A$	quenching
${}^3A^* \longrightarrow A$	triplet decay

INITIATION & PROPAGATION

$I\cdot + M \longrightarrow IM\cdot$	initiation
$2I\cdot \longrightarrow I{-}I$	recombination
$I\cdot + O_2 \longrightarrow IO_2\cdot$	O_2 addition
$P\cdot + M \longrightarrow PM\cdot$	propagation
$P\cdot + O_2 \longrightarrow PO_2\cdot$	O_2 addition
$P\cdot + I\cdot \longrightarrow PI$	I-termination

A = Photoinitiator or photosensitizer in ground state.
${}^1A^*$= Photoinitiator or photosensitizer in singlet excited state.
${}^3A^*$= Photoinitiator or photosensitizer in triplet excited state.
${}^3[A{-}{-}{-}HR]^*$ = Activated complex in triplet excited state ("exciplex").
R = Accelerator or coinitiator.
RX = Halogenated accelerator or coinitiator.
$I\cdot$ = Initiator radical, e.g., $B\cdot$, $C\cdot$, $AH\cdot$, $R\cdot$, $X\cdot$.
$X\cdot$ = Halogen radical, e.g., $Cl\cdot$.
M = Monomer
P = Oligomer
Q = Quenching agent, e.g., O_2.

APPENDIX 2

CATIONIC POLYMERIZATION PHOTOINITIATION MECHANISMS

Photolysis of Diaryliodonium Salts

Major

$$Ar_2I^+X^- \xrightarrow{h\nu} [Ar_2I^+X^-]^* \qquad (a)$$

$$[Ar_2I^+X^-]^* \longrightarrow Ar\text{-}I^{+\cdot} + Ar\cdot + X^- \qquad (b)$$

$$Ar\text{-}I^{+\cdot} + M\text{-}H \longrightarrow Ar\text{-}I^+\text{-}H + M\cdot \qquad (c)$$

$$Ar\text{-}I^+\text{-}H \longrightarrow Ar\text{-}I + H^+ \qquad (d)$$

Minor

$$[Ar_2I^+X^-]^* + M\text{-}H \longrightarrow [Ar\text{-}MH]^+ + ArI + X^- \qquad (e)$$

$$[Ar\text{-}MH]^+ \longrightarrow Ar\text{-}M + H^+ \qquad (f)$$

Initiation by Diaryliodonium Salts & Propagation

$$Ar_2I^+X^- \xrightarrow[MH]{h\nu} ArI + Ar\cdot + M\cdot + HX \qquad (a)$$

$$M + HX \longrightarrow HM^+\,X^- \qquad (b)$$

$$M + HM^+X^- \longrightarrow HMM^+X^- \qquad (c)$$

$$nM + HMM^+X^- \longrightarrow H\text{-}M(M)^+_{n+1}\,X^- \qquad (d)$$

Photolysis of Triarylsulfonium Salts

$$Ar_3S^+\,X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \qquad (a)$$

$$[Ar_3S^+X^-]^* \longrightarrow Ar_2S^{+\cdot} + Ar\cdot + X^- \qquad (b)$$

$$Ar_2S^{+\cdot} + M\text{-}H \longrightarrow Ar_2S^+\text{-}H + M\cdot \qquad (c)$$

$$Ar_2S^+\text{-}H \longrightarrow Ar_2S + H^+ \qquad (d)$$

Ar = Aryl moiety, e.g. phenyl, 4-methylphenyl, etc.
$[Ar_2I^+X^-]^*$ = Diaryliodonium salt in excited state.
$[Ar_3S^+X^-]^*$ = Triarylsulfonium salt in excited state.
X = Anion, e.g., SbF_6^-, AsF_6^-, PF_6^-, BF_4^-, etc.
M = Monomer