

Stabilization of UV-Curable Vinyl Compositions by Transition Metal Compounds

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Synopsis

A UV-curable composition, which has a shelf life of greater than six months at 60°C for bonding or coating glass surfaces, was developed. The formulation consists of a dimethacrylate monomer, a methacryltrialkoxysilane, a photoinitiator, MEHQ, DLTDP, a water scavenger, and FeCl₃. In the absence of FeCl₃, gelation occurs within 24 hr at 25°C. Gelation is caused by the formation of a crosslinked vinyl addition polymer having a methacrylate diester/silane monoester mole ratio of 20:3. Analogous stability is achieved if instead of FeCl₃ a number of heavy metal compounds are used, including CrCl₃, CoCl₂, NiCl₂, RuCl₃, Pr(fod)₃, and Eu(fod)₃. Nontransition metal compounds, e.g., AlCl₃, BCl₃, and SnCl₂, are poor or ineffective stabilizers. Gelation is initiated by free radicals. When MEHQ and DLTDP are present, less Fe³⁺ is converted to Fe²⁺ than in their absence. This indicates that a complex interaction is operating among these substances. A scheme is presented in which recycling of Fe³⁺ and phenolic and thioether antioxidants is proposed.

INTRODUCTION

The area of vinyl monomer stabilization has received far less attention in comparison to polymer stabilization and presents a challenging problem to the producers of monomers and monomer compositions. The reactivity of vinyl monomers is used to advantage in a large number of applications in the coatings and adhesives field. Vinyl formulations can be polymerized efficiently by thermal or radiative methods. However, the reactivity of these substances towards spontaneously generated free radicals requires that stabilizers be present during storage. It is frequently found that combinations of stabilizers work synergistically; for example, the interaction of phenolic and thioether antioxidants has been described.^{1,2} In this article, it will be shown that transition metal compounds, e.g., FeCl₃, can provide long-term stability to vinyl compositions in the presence of phenolic and thioether antioxidants. The presence of these stabilizers does not interfere with rapid curing under UV.

EXPERIMENTAL

Materials

Organic Chemicals

Ethoxylated bisphenol-A dimethacrylate (Sartomer); γ -(methacryloxy)propyltrimethoxysilane (Union Carbide); trimethyl orthoformate, benzyl chloride, 2-chlorobutane, 2,6-di-*tert*-butyl-3-methylphenol, *p*-methoxyphenol, *p*-toluenesulfonic acid (Aldrich), dilauryl thiodipropionate (American Cyanamid), 2,2-dimethoxy-2-phenylacetophenone (Ciba-Geigy), and Vanox SKT (R.T.

Vanderbilt) were used without purification. All solids gave acceptable melting points. All of these compounds yielded IR spectra and NMR spectra that were consistent with the manufacturers' labels. Reagent grade methanol, chloroform, and carbon tetrachloride were used.

Metallo-Organic and Inorganic Chemicals

Eu(fod)₃ and Pr(fod)₃ were obtained from Aldrich. All other inorganic compounds were reagent grade and used without purification.

Abbreviations

EBPADMA: ethoxylated bisphenol-A dimethacrylate.

MEHQ: *p*-methoxyphenol.

DLTDP: dilauryl thiodipropionate.

fod: *tris*(6,6,7,7,8,8-heptafluoro-2,2-dimethyl-2,5-octanedionato).

Vanox SKT: 2,5-di-*tert*-butyl-4-hydroxyhydrocinnamic acid with 1,3,5-*tris*(2-hydroxyethyl)-*s*-triazine-2,4,6(1H,3H,5H)-trione.

METHODS

Formulation work was done under red light. A typical formulation is described in Table I. Samples of 25 ml were bottled in 125-ml, amber screw-top bottles to provide a large head space. IR spectra were taken on a Perkin-Elmer model 299 as KBr pellets, nujol mulls, or thin films. NMR spectra were taken with a Varian model EM 360A using CCl₄ or CDCl₃ with TMS as internal standard. Atomic absorption measurements were made with a Perkin-Elmer model 403. Viscosity determinations were performed with a Brookfield viscometer model LVT equipped with a small sample adapter at 25 ± 0.2°C. Analysis for ferrous iron was made with a modification of the *o*-phenanthroline method with NH₂OH as reductant³; the solvent was acetone-water, 9:1. Spectrophotometric measurements were made with a Cary 14. MEHQ was assayed at 420 nm after reaction with NaNO₂ in acetic acid-methanol, 4:6 (ref. 4). Elemental analysis was performed by Herron Testing Laboratories, Inc., Cleveland, OH. The adequacy of UV cure of the formulation was monitored by irradiating a small sample be-

TABLE I
Composition of UV Curable Formulation

Component	Weight %
EBPADMA	81.5
γ(Methacryloxy)propyltrimethoxysilane	13.0
2,2-Dimethoxy-2-phenylacetophenone	2.0
Trimethyl orthoformate	2.0
Dilauryl thiodipropionate	0.30
MEHQ	0.30
Methanol	0.80
Fe ³⁺ as FeCl ₃	60 ppm
<i>p</i> -Toluenesulfonic acid	10 ppm

tween two glass slides at a distance of 1 cm from a Sylvania 4T5BLB lamp for 1 min. A tight bond was evidence of cure. Films on glass slides were prepared by UV irradiation through the slide of a "sandwich" consisting of glass slide, formulation, and Mylar tape. Adhesion of cured films to glass was estimated by immersion of coated slides for 5 min in a 50°C water bath followed by 5 min in a 50°C oven. The films were then scraped with a razor blade. The hardness of cured films was estimated with a Brumbaugh pencil hardness tester.

RESULTS

Isolation of Crosslinked Polymer from Incompletely Gelled Adhesive

In the development of UV-curable coatings for glass surfaces, the following was found to be stable as a two-part system, but extremely unstable as a one-part system (see Table I). Part 1 is a EBPADMA which contains 300 ± 25 ppm of MEHQ added by the supplier. Part 2 is composed of the silane, 2,2-dimethoxyphenylacetophenone, trimethyl orthoformate, *p*-toluenesulfonic acid, MEHQ, and DLTD. The particular dimethacrylate monomer was chosen because it contributes low volatility and high viscosity to the formulation and desirable optical properties and hardness to UV-cured films. The organosilane was added to enhance adhesion to glass. Both parts were stable for two months at 60°C showing no increase in viscosity. However, when combined, gelation occurred within 24 hr at 25°C. Gelation was not prevented by omission of the photoinitiator, variation of manufacturing lots of silane or diester, or by substitution for MEHQ by the more hindered phenolics, 2,6-di-*tert*-butyl-3-methylphenol or Vanox SKT. The concentration of MEHQ did not change during the first 2 hr after the mixture was made. Beyond this stage, the presence of polymers caused sufficient turbidity to prevent further measurements. The mixture, as well as the individual parts, was bottled with a head space of 100 ml to provide adequate O₂ content.⁵

Within 24 hr at 25°C, an organogel was obtained which maintained a soft consistency for many months. The gel (6.33 g) was extracted five times with 50-ml portions of CCl₄ which permitted swelling to release unpolymerized materials and any linear polymers. After filtration, the swollen crosslinked particles were collapsed and concentrated with MeOH. After five cycles, the crosslinked material was dried to constant mass at 45°C to yield 0.64 g (10% yield).

The IR spectrum (KBr) of the crosslinked polymer was quite similar to that of films of the fully UV-cured formulation showing bands at 3020 (aryl C—H stretch); 1607 (vinyl C=C stretch); 1500 (aryl C=C stretch); 1380, 1360 (gem-dimethyl C—H bend); and 820 cm⁻¹ (*p*-substituted aromatic C—H bend) for EBPADMA. A band at 1095 cm⁻¹ (Si—O—C) indicated the presence of the silane. Both the silane monoester and the methacrylate diester had a strong band at 1717 cm⁻¹ (ester C=O). In contrast to the uncured adhesive, the spectrum of the crosslinked polymer exhibited markedly diminished absorption at 1640, 1455, 1403, and 640 cm⁻¹, showing the loss of carbon-carbon double bonds. Elemental analysis of the crosslinked material revealed 69.8% C, 7.07% H, and 0.84% Si. A crosslinked vinyl addition polymer with diester/silane mole ratio of 20:3 requires 69.9% C, 7.10% H, and 0.86% Si. The mole ratio of these components in the original formulation is 3.45:1. These results indicate that

gelation was caused by vinyl polymerization and not by polysiloxane formation.

Effect of Transition Metal Compounds and Organic Halides on Gelation

Analysis of EBPADMA and the silane by atomic absorption spectroscopy revealed that both raw materials contained 1–5 ppm of Fe, Mn, and Cu. Since trace levels of transition metal ions have been reported to be involved in the autooxidation of low-molecular-weight organics,¹ 60 ppm of Fe³⁺, as FeCl₃, was added to the one-part formulation with the expectation that the gelation rate would be increased versus control. However, gelation was prevented entirely and the stability was increased to greater than six months at 60°C. The gel time was approximately proportional to the FeCl₃ concentration, since 10 ppm of Fe³⁺ protected against gelation for only three weeks at 60°C. Other compounds which were effective stabilizers at $1 \times 10^{-3}M$ include FeBr₃, CrCl₃, MnCl₂, CoCl₂, NiCl₂, and RuCl₃. These compounds were added as solutions in MeOH (see Table II). In analogous fashion, Pr(fod)₃ and Eu(fod)₃ in CCl₄ also led to marked stabilization. Compounds that were partially effective include AlCl₃ and CuCl₂. In contrast, nontransition metal compounds such as BCl₃ and SnCl₂ were not effective. On testing the solvents, methanol was completely ineffective at 1% (v/v), while the addition of CCl₄ was partially effective against gelation at 60°C. For a series of organic halides at 1% (v/v), the order of decreasing effectiveness was benzyl chloride > CCl₄=CHCl₃ > 2-chlorobutane (see Table III). These organic

TABLE II
Effect of Addition of Inorganic Compounds to Vinyl Formulation to Test as Stabilizers against Gelation

Compound ^a	Solvent ^b	Gel time, days ^c	
		60°C	25°C
—	—	1 G	1 G
—	Methanol	1 G	1 G
AlCl ₃	Methanol	165 L	165 V
CrCl ₃	Methanol	165 L	165 L
MnCl ₂	Methanol	195 L	195 L
FeCl ₃ *	Methanol	21 G	—
FeCl ₃	Methanol	195 L	195 L
FeBr ₃	Methanol	195 L	195 L
CoCl ₂	Methanol	165 L	165 L
NiCl ₂	Methanol	165 L	165 L
CuCl ₂	Methanol	165 L	165 V
RuCl ₃	Methanol	165 L	165 L
SnCl ₂	Methanol	—	14 G
—	CCl ₄	165 G/2	1 G
Eu (fod) ₃	CCl ₄	165 L	165 L
Pr (fod) ₃	CCl ₄	165 L	165 L
BCl ₃	CH ₂ Cl ₂	3 G	3 G

^a Duplicate samples for each temperature, inorganic compound concentration was $1 \times 10^{-3}M$ except* where the concentration was $1 \times 10^{-4}M$.

^b Final solvent concentration was 1% (v/v).

^c (G) gel; (G/2) bottom half of samples gelled; (L) liquid; (V) increased viscosity.

TABLE III
Effect of Organic Halides as Stabilizers Against Gelation

Compound, 1% (v/v) ^a	Gel time	
	days, 60°C ^c	days, 25°C
—	1 G	1 G
Methanol	1 G	1 G
Benzyl chloride ^b	135 L	1 G
CCl ₄ ^b	135 G/2	1 G
CHCl ₃ ^b	135 G/2	1 G
2-chlorobutane ^b	5 G	1 G

^a Duplicate samples for each temperature.

^b Molar concentrations $\sim 0.1M$.

^c (G) gelled; (G/2) bottom half of sample gelled; (L) liquid.

halides were tested at concentrations approximately 100-fold higher than those of the inorganic additives.

Interactions Involving the Stabilizers

In the absence of FeCl₃, MEHQ at 3000 ppm ($2.4 \times 10^{-2}M$) and DLTPD at 3000 ppm ($5.8 \times 10^{-3}M$) were totally ineffective in preventing gelation. In the absence of MEHQ and DLTPD, FeCl₃ at $1 \times 10^{-3}M$ provided only three weeks' stability at 60°C. However, when these three substances were all present at the levels shown above, the formulation was stable for greater than six months at 60°C. This clearly demonstrates a complex interaction. Synergistic effects between phenolic and thioether antioxidants have been described.^{1,2} Additional evidence to support the synergism between FeCl₃, MEHQ, and DLTPD comes from analysis of the percentage of Fe³⁺ converted to Fe²⁺, as shown in Table IV. In the complete formulation, after ten days at 60°C, 3.8% of the original ferric ions was turned over. However, under parallel conditions in which MEHQ and DLTPD were omitted, there was a 23% conversion of Fe³⁺ to Fe²⁺.

Bulk Properties of Cured Films

The presence of FeCl₃, other transition metal compounds, MEHQ and DLTPD at the concentration described earlier, did not interfere with the rapid curing under UV or adhesion of the films to glass. The films have a relative hardness of *F* on the Brumbaugh pencil hardness scale and were optically transparent.

TABLE IV
Effect of Stabilizer System on Gel Time and % Yield of Ferrous Ion

Stabilizers ^a	Gel time, ^b 60°C	% Yield Fe ²⁺ ,
		10 days at 60°C ^c
FeCl ₃ , MEHQ, DLTPD	>6 months, L	3.8
FeCl ₃	3 weeks, G	23

^a Concentrations: FeCl₃, $1 \times 10^{-3}M$; MEHQ, $2.4 \times 10^{-2}M$; DLTPD, $5.8 \times 10^{-3}M$.

^b (L) Liquid; (G) gelled.

^c Fe²⁺ determined with *o*-phenanthroline, ref. 3.

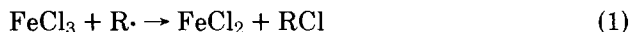
DISCUSSION

The mode of gelation and the role of transition metal compounds such as FeCl_3 in preventing gelation will now be discussed. It will be recalled that the vinyl formulation comprised of the methacrylate diester, the trialkoxy monomethacrylsilane, the water scavenger, photoinitiator, MEHQ, and DLTDP is an extremely unstable system which forms a soft organogel within 24 hr on standing in the dark at 25°C. From the gel, an insoluble polymeric material was isolated which exhibited markedly diminished IR absorption at frequencies that are characteristic of ethylenic carbon-carbon double bonds. Both IR and elemental analyses indicate that this polymer is composed of methacrylate diester and trialkoxy monomethacrylsilane moieties. The elemental analysis is consistent with a vinyl addition polymer with a mole ratio of methacrylate diester/silane monoester of 20:3. Methacrylates are known to undergo vinyl polymerization by three routes—free radical, cationic, or anionic—depending on the presence of specific initiator species.⁶

If gelation is initiated by free radicals, then the effectiveness of the organic halides in Table III as gelation inhibitors would be related to the stability of the respective free radicals formed upon atom abstraction. A stable radical would be expected to undergo reaction with greater selectivity and be a poorer chain initiator than an unstable radical. Benzyl chloride is known to undergo H· abstraction to yield the α -chloro-benzyl radical,⁷ which is extensively stabilized by resonance. CCl_4 and CHCl_3 lose Cl· and H·, respectively, to form $\cdot\text{CCl}_3$.⁸ This species is believed to be stabilized by delocalization of the unpaired electron into molecular orbitals involving the three bonded chlorines.⁹ Finally, the ineffectiveness of 2-chlorobutane can be rationalized in terms of the poorly stabilized secondary radical which would result from atom abstraction.

On the other hand, cationic polymerization can be ruled out because the presence of Lewis acids such as AlCl_3 and BCl_3 did not cause the gelation rate to increase versus control. In fact, AlCl_3 was observed to be a partial stabilizer. Lewis acids are known to be effective in promoting the cationic mode of vinyl polymerization in the presence of compounds containing active hydrogen, such as alcohols.⁷ The formulation contains 1% (v/v) methanol. *p*-Toluenesulfonic acid is present at about $1 \times 10^{-5}M$ as part of the water scavenger system; trimethyl orthoformate is also present. However, this strong acid can be said to play no role as a catalyst promoting cationic polymerization. The anionic mode is extremely unlikely because of the requirement for strongly basic initiator species, none of which appear to be present. Consequently, the results are consistent with gelation being triggered by free radicals.

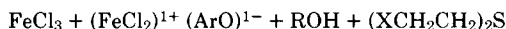
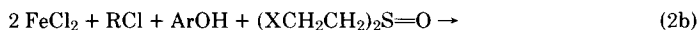
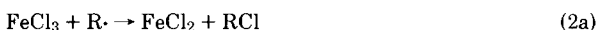
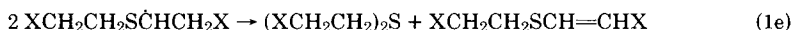
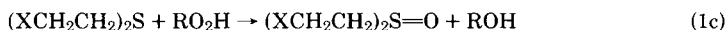
On the basis of the argument presented, the action of FeCl_3 as a stabilizer in the defined monomer formulation can be proposed as



This is consistent with the account of Bengough and Chowdry,¹⁰ who reported that the formation of FeCl_2 from the reaction of $10^{-3}M$ FeCl_3 with free radicals generated from the polymerization in DMF of vinyl chloride in the presence of AIBN. Similarly, free radical polymerization of acrylonitrile, methacrylonitrile, and styrene in DMF in the presence of FeCl_3 yielded FeCl_2 .¹¹ In this case, the rate of polymerization was retarded by FeCl_3 .

It is interesting to compare the activities of the transition metal compounds

and the organic halides as stabilizers against gelation. The transition metal compounds are effective at both 25 and 60°C at a concentration of $1 \times 10^{-3}M$. Under these conditions, formulations are stabilized against gelation in excess of six months. In contrast, the organic halides were effective at 60°C but not at 25°C and at a concentration of 1% (v/v), which corresponds to approximately 0.1M. These results suggest that the two classes of stabilizers must function by different mechanisms. The halides evidently have a much larger activation energy requirement than the transition metal compounds.



Scheme I

A scheme is proposed to account for the synergism involving the phenolic, thioether, and transition metal compound stabilizer species (see scheme I). In step (1a), the spontaneously generated free radical species $R \cdot$ is trapped by O_2 to yield $RO_2 \cdot$. In step (1b), the phenolic antioxidant reduces $RO_2 \cdot$ to generate a hydroperoxide RO_2H and $ArO \cdot$.¹ Steps (1c)–(1e) show the reaction of the thioether with RO_2H to generate the sulfoxide and alcohol, the reaction of the thioether with $ArO \cdot$ to regenerate the phenolic species, and the disproportionation of the thioether radical which partially regenerates the original thioether and a dehydrogenated thioether product.² In step (2a), $FeCl_3$ is reduced to $FeCl_2$ by reaction with $R \cdot$.⁸ Step (2b) shows the net reaction of $FeCl_2$, RCl , $ArOH$, and sulfoxide to regenerate $FeCl_3$ and the thioether. This is a composite step which is based on the known ease of reduction of sulfoxides by a number of mild reducing agents, for example, $TiCl_3$,¹² $CrCl_2$,¹³ and P_4S_{10} .¹⁴ This scheme, which accounts for the complex interactions operating among the three stabilizer species, is attractive because of the regeneration of these species. It is consistent with the synergism previously reported between the phenolic and thioether antioxidants² and a new type of synergism linking the transition metal ion with the other two types of stabilizers.

CONCLUSION

This article reports the utilization of transition metal compounds in conjunction with phenolic and thioether antioxidants to provide stability in excess of six months at 60°C for a UV-polymerizable vinyl monomer composition. It is believed that this is the first description of the usage of such a ternary stabilizer

system for monomers.* A scheme is presented to explain the complex interactions linking the three types of stabilizer species. It is anticipated that this stabilizer system will find application in other polymerizable vinyl compositions.

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References

1. J. R. Shelton, *Polymer Stabilization*, W. L. Hawkins, Ed., Wiley-Interscience, New York, 1972, chap. 2, pp. 80–116.
2. C. R. H. I. DeJonge, E. A. Giezen, F. P. B. van der Maeden, W. G. B. Huysmans, W. J. deKlein, and W. J. Mijs, *Stabilization and Degradation of Polymers*, D. L. Allera and W. L. Hawkins, Eds., American Chemical Society, Washington, DC, 1978, pp. 399–425.
3. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., Longmans, London, 1961, p. 787.
4. Personal communication, Sartomer Company, West Chester, PA.
5. R. G. Caldwell and J. L. Ihrig, *J. Am. Chem. Soc.*, **84**, 2878 (1962).
6. K. J. Saunders, *Organic Polymer Chemistry*, Chapman and Hall, London, 1973, p. 15.
7. G. J. Gleicher, *Tetrahedron*, **30**, 935 (1941).
8. E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart, and Winston, New York, 1959, p. 743.
9. C. J. H. Schutte, *J. Chem. Phys.*, **51**, 4678 (1969).
10. W. I. Bengough and N. M. J. Chowdry, *J. Chem. Soc. Faraday Trans. 1*, **68**, 1807 (1976).
11. C. H. Bamford, A. D. Jenkins, and R. Johnson, *Proc. R. Soc. London Ser. A*, **239**, 214 (1957).
12. L. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 5, Wiley, New York, 1975, p. 670.
13. Y. Akita, M. Inaba, H. Uchida, and A. Ohta, *Synthesis*, **11**, 792 (1977).
14. I. W. J. Still, S. K. Hasan, and K. Turnbull, *Can. J. Chem.*, **56**, 1423 (1978).
15. P. A. Small and D. G. M. Wood, Br. Pat. 1,339,014 (1973).
16. M. Braid, U.S. Pat. 4,090,970 (1978).

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* It is interesting to note that ternary stabilizer systems comprised of a transition metal ion or compound, a phenol and a thioether have been reported to stabilize polypropylene¹⁵ and lubricating oils.¹⁶ However, polypropylene and lubricating oils, unlike vinyl monomers, do not possess carbon-carbon double bonds. Therefore, there may be similar mechanisms involved in the stabilization of saturated and unsaturated materials.