

Study of Reactive Diluent for Air-Dried Alkyd Paint

SATORU ENOMOTO, HITOSHI TAKITA SADA O NISHIDA,
HISAUKI WADA, YUTAKA MUKAIDA, and MIKIRO YANAKA, *Kureha
Chemical Industry Co., Ltd., Tokyo Research Laboratory, Tokyo, Japan*

Synopsis

The conventional air-dried alkyd resin is generally used with 30% to 40% of some organic solvent which dissipates into atmosphere after painting and becomes a factor of air pollution. A reactive diluent was investigated to reduce the content of the organic solvent and to manufacture a high-solid or superhigh-solid paint. 1,1-Bis(1'-methyl-2'-vinyl-4',6'-heptadienoxy)ethane was found to be suitable as the reactive diluent among the investigated compounds. A small addition of this compound to alkyd paint reduced the content of solvent to less than 15% with a conventional alkyd resin of high molecular weight (high-solid type); and, further, a superhigh solid paint (5% solvent) could be manufactured when this compound was added to a superlong oil-length alkyd resin of low molecular weight.

INTRODUCTION

Most paints, except for a few, are used with some organic solvents to facilitate their paintability by lowering the viscosity. The solvents, however, dissipate into atmosphere after painting. This conventional painting method is not only a factor of air pollution¹ but also a waste of valuable chemical petroleum products. Recently, some efforts have been made to replace the organic solvent with water, coating with powder resin, and using curable monomer by irradiation with ultraviolet light or electron beam. But paint that uses water as solvent does not have a sufficient drying rate or surface gloss because of the slow evaporation and the poor solubility of water, and some paints need special instruments.

The organic solvent evaporating into the atmosphere can be recovered during the painting operation in a special, closed system, but the trouble occurs mainly from the common operation in an open system, where the usual, popular method which evaporates the organic solvent is air drying. A better method could be to increase the solid content of this conventional paint by modifying the resin and adding a new reactive diluent while returning excellent paint properties. The concept, called high-solid paint, would help to increase the thickness of the painted film by one painting operation in addition to reducing the waste of organic solvent into the atmosphere and saving a valuable resource. This report will mention several organic compounds as new reactive diluent for the usual alkyd paint modified with drying oils.

BASIC STRUCTURE OF REACTIVE DILUENT

Properties Required of Curable Diluent at Room Temperature

The resins of conventional paints were classified into two main groups from the point of their curing mechanisms at room temperature: The first one did

not need any special curing agent, and the second was cured with a reactive hardener added just before painting because of the short pot life. Alkyd paint modified with drying oil was most popular and convenient among resins in the first group because of easy painting. The curing mechanism, i.e., the formation of three-dimensional crosslinked structure, was based on the chemical behavior of the modified drying oil. The carbon-carbon double bond produced a peroxide by absorbing an oxygen molecule, and the decomposed radical initiated the crosslinking polymerization. A so-called dryer composed of some metal naphthanates was added to the paint in the manufacturing process to accelerate the curing rate at air drying time.²

This simple curing mechanism was quite attractive for studying an expected reactive diluent. It was hard to use drying oil as a reactive diluent in the same manner as a organic solvent because of the high viscosity and slow curing rate. For example, linseed oil was used as the thermally polymerized standing oil or the oxidatively polymerized boiled oil after improving the curing rate. The ideal reactive diluent should be nonvolatile and reactive just like the alkyd resin modified with drying oil and also have a viscosity similar to that of the solvent.

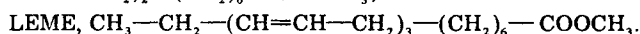
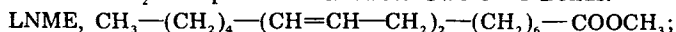
Curable Organic Compounds

Several unsaturated compounds were studied to find the curing conditions of the carbon-carbon double bonds based on the mechanism of auto-oxidation. The rate of formation and decomposition of the peroxide was approximated from the observed value of oxygen absorbed by the compound. The curing rate was estimated qualitatively from the time which was required for a thinly painted film on a glass plate to arrive at the state of "set to touch." The following compounds were used:

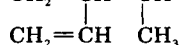
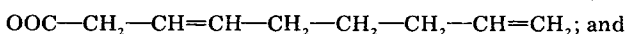
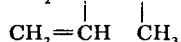
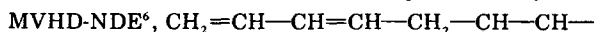
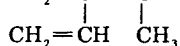
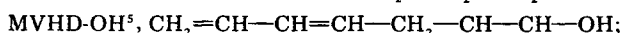
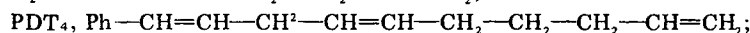
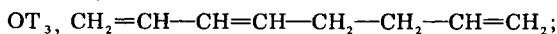
Isolated C=C Bond.



Active CH_2 Group Inserted Between Two C=C Bonds.



Conjugated C=C Bond and Isolated C=C Bond.



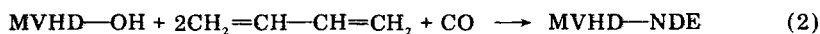
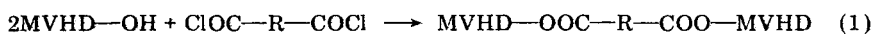
The results are shown in Table I and Figure 1. Among the first three compounds, the amount of absorbed oxygen seemed to depend on the number of double bonds, as LEME had the highest and OME had the lowest number. In spite of the high absorption among all the samples, LEME could not stand on the practical position of an expected reactive diluent because of the slow curing rate.

This could be explained by the resonance stabilization of the produced allyl radical.²

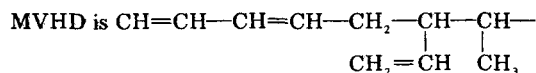
The compounds having conjugated double bonds showed different behavior from the ones which contained only an isolated double bond or an active CH₂ group inserted between two double bonds. OT absorbed oxygen less than LNME, but the curing rate was better than that of LEME, and conjugated double bonds would increase the curing rate.

OT was actually inadequate as an expected reactive diluent from the point of both volatility and unpleasant smell. PDT was prepared to decrease volatility by addition of a phenyl group to OT. The addition increased the oxygen absorption and the curing rate, but still could not remove the unpleasant smell. The dimer of OT, i.e., 1,5,7,10,15-hexadecapentane,⁷ also increased the curing rate, but the unpleasant smell was not improved by only the dimerization, which contributed largely to raising the boiling point.

An oxygen atom was introduced into the pure hydrocarbon compounds to reduce their smells. The oxygen absorption of MVHD-OH was rather low, but the time of "set to touch" was the same as that of PDT, and it smelled like a perfume. The hydroxy group of MVHD-OH was utilized to increase the molecular weight and to improve the smell, keeping the reactive double bond; esterification, joint reactions with TDI and phosgene, and acetal formation were all tried:



where



The usual esterification with carboxylic acid and alcohol could not be applied to the secondary hydroxy group of MVHD-OH at a temperature below 100°C without polymerization, and reaction (1) at room temperature was used to prepare the succinate and the terephthalate. These esters gave excellent curing rates and were completely odorless, but slightly too viscous to be expected reactive diluents. The reaction shown in eq. (2) was useful for uncomplicated

TABLE I
Set-to-Touch Time of Various Unsaturated Compounds^a

| Compound | Time to "set to touch" (25°C) | Viscosity (25°C), cst | Boiling point, °C/mm Hg | Odor |
|----------|-------------------------------------|--------------------------|----------------------------|------|
| OME | 14 days | 6.27 | 160-162/2-3 | none |
| LNME | 7 days | 5.57 | 168-170/1 | none |
| LEME | 7 days | 4.87 | 177-180/3.5 | none |
| OT | 4-5 hr | low | 125-130/760 | bad |
| PDT | 1 day | low | 125-128/2 | bad |
| MVHD-OH | 1 day | 6.85 | 60-65/1 | bad |
| MVHD-NDE | 15 hr | 5.89 | 140-145/3 | none |
| MVHD-ACE | 2-3 hr | 8.63 | 144-148/2 | none |

^a Dryer Co naphthanate, 1 mole %; thickness of coated film, 100 microns.

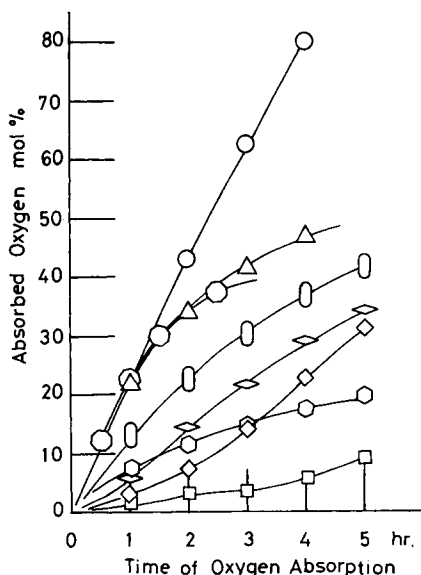
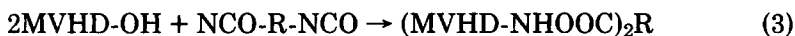


Fig. 1. Absorption of oxygen for various unsaturated compounds: (—□—)OME; (—△—)LNME; (—○—)LEME; (—○—)OT; (—◇—)PDT; (—○—)MVHD-OH; (—◇—)MVHD-NDE; (—○—)MVHD-ACE.

preparation of an ester of unsaturated aliphatic acid and the unsaturated secondary alcohol. This esterification improved MVHD-OH with regard to raising the boiling point and becoming odorless. The addition of butadiene to MVHD-OH increased the number of isolated double bonds and decreased the concentration of the conjugated double bond in MVHD-NDE, on the other hand, and this result still accelerated the curing time even while reducing the initial value of the absorbed oxygen.

Joint Reactions with TDI and Phosgene



The stoichiometric reaction as shown in eq. (3) was impossible, and the unavoidable side reaction between the formed urethane bond and the unreacted isocyanate group made the product rather viscous, but the carbonate of eq. (4) was an expected reactive diluent, having a viscosity of 17.2 cst.

Acetal Formation



Acetaldehyde, butylaldehyde, and octylaldehyde were allowed to react with MVHD-OH, the physical properties of the prepared acetals are listed in Table II. Their viscosities increased with the extension of the alkyl group of the aldehydes and had a tendency for thermal polymerization during distillation. Vacuum distillation was limited to MVHD-ACE, and the other acetals were purified on a silica gel column eluting with a solvent. The acetal formations were confirmed by IR spectra, NMR spectra, and molecular weights.

STUDY OF MVHD-ACE

The study was focused on MVHD-ACE [(MVHD-O)₂CHCH₃] because it satisfied the necessary conditions for an expected reactive diluent, in addition to the easiest preparation among the prepared acetals, and auto-oxidative gelation occurred quickly after 2 hr from the beginning of oxygen absorption.

Cure of MVHD-ACE by Air Drying

The temperature dependence of the curing rate and the structural changes in the curing process were studied. MVHD-ACE was cured with the help of a mixed drying agent containing both Co naphthanate and Pb naphthanate (weight ratio of Co/Pb was 0.5); and the amount used was 0.05 phr. MVHD-ACE was coated on a glass plate with a doctor blade, and the thickness was adjusted to be from 10 to 15 microns. Figure 2 represents the relation between the curing temperature and the time of set to touch. The time decreased linearly with increase in temperature, and MVHD-ACE had a practically tolerable curing rate because it arrived at the state of set to touch within 4 hr at room temperature after coating.

Figure 3 shows the infrared spectral changes of MVHD-ACE and a commercial alkyd resin modified with a drying oil. The bands at 900 and 1000 cm⁻¹ were assigned to the CH out-of-plane modes of the conjugated part, and the mode of the vinyl group appeared at 950 cm⁻¹ in spectrum A of uncured MVHD-ACE. Spectrum B shows that the band at 1000 cm⁻¹ became weak and that any significant change due to the oxidation was hardly observed; and the initial cure, i.e., the state of set to touch, would occur between the conjugated part. Both bands of the conjugated part were reduced significantly in the curing process, and the stretching modes of the hydroxy group and carbonyl group appeared clearly at 3600 cm⁻¹ and 1700 cm⁻¹, respectively, in spectrum C. As spectrum E of the cured alkyd resin had the same tendency, the second cure of MVHD-ACE would proceed by the same mechanism like the alkyd resin.

The curing process of MVHD-ACE was also studied by the change in refractive index.⁸ The initial value of uncured MVHD-ACE became smaller linearly with higher temperature, but it increased during the curing process, and the change

TABLE II
Physical Properties of (MVHD-O)₂CH-R

| | Aldehyde R—CHO | | |
|-----------------------------|--------------------------|-------------------------------|--------------------------------|
| | CH ₃ | C ₃ H ₇ | C ₇ H ₁₅ |
| Boiling point, °C/mm Hg | 315–320/760 144–148/2 | — | — |
| Viscosity (25°C), cts | 8.63 | 22.1 | 19.2 |
| Refractive index n_D^{25} | 1.4908 | 1.4846 | 1.4834 |
| Density d_4^{15} | 0.9025 | 0.9071 | 0.8884 |
| Molecular weight | | | |
| obsd (VPO) | 349 | 365 | 413 |
| calcd | 330 | 358 | 400 |

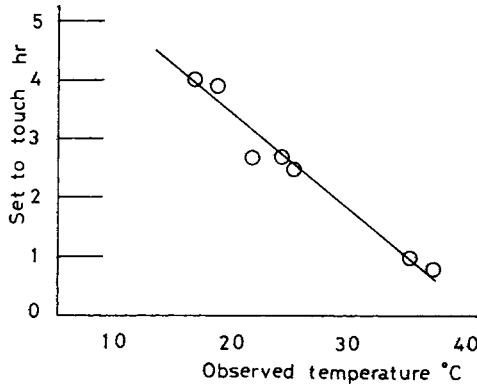


Fig. 2. Relation between set to touch and temperature.

became more rapid with increase in observed temperature. The state of set to touch required a refractive index above 1.497, as shown by the arrow head in Figure 4.

Compatibility of MVHD-ACE with Various Resins

The compatibility of MVHD-ACE was an important property for its use as a reactive diluent. Resin, 50 weight parts, was dissolved in 50 weight parts MVHD-ACE to check the solubility, and the mixture was cured into a thin film to observe the transparency. These visual tests to determine the qualitative compatibilities of solutional and solid states were classified into the following four groups:

| <u>Compatibility</u> | <u>Solution</u> | <u>Solid</u> |
|----------------------|-----------------|-----------------|
| very good | soluble | clear |
| good | soluble | slightly opaque |
| fair | partially | opaque |
| bad | insoluble | separted |

The results are shown in Tables III and IV, respectively. Alkyd resins modified with drying oils, except the short oil length-type modified with soybean oil, were generally compatible with MVHD-ACE, and this was improved by further modification with phenol. MVHD-ACE was difficult to apply to epoxy resin because of the different curing mechanism; and also a suitable selection of polyol and isocyanate compound should be considered when using MVHD-ACE for polyurethane. Resins containing only carbon and hydrogen atoms, such as petroleum resin and 1,2-polybutadiene, were most preferable with MVHD-ACE, and the cured product showed very excellent appearance similar to that of the alkyd resins.

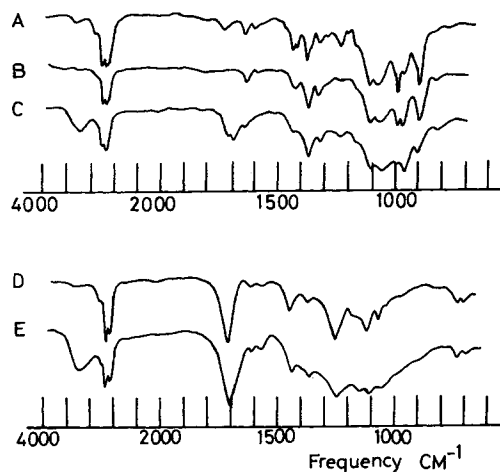


Fig. 3. Infrared spectral changes of MVHD-ACE and modified alkyd resin with soybean oil.

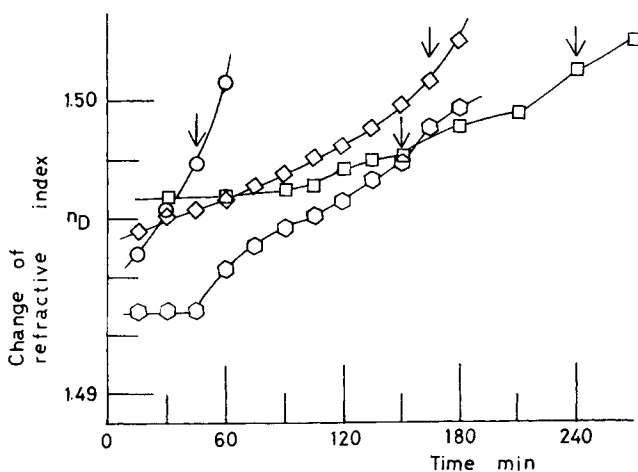


Fig. 4. Changes of refractive index of MVHD-ACE: (—□—)16°C; (—○—)25°C; (—◇—)21°C; (—○—)37°C.

Basic Application of MVHD-ACE for Alkyd Paint

MVHD-ACE was evaluated practically as a reactive diluent by preparing white paint. Table V shows the results obtained with a conventional alkyd resin of high molecular weight. The viscosity values which were observed by a Ford cup No. 4 were adjusted to be from 70 sec to 80 sec for easy painting. The total resin was composed of solid alkyd resin, MVHD-ACE, and heat-bodied linseed oil (No. 5 and No. 6); the ratio of total resin to pigment was 1:0.98. From the point of paintability, it was difficult to reduce the content of solvent to less than 30% in case of only a conventional alkyd resin of high molecular weight. As shown in No. 3 and No. 4, the volatile content could be reduced to 15% or 5% by replacing of the alkyd resin with MVHD-ACE. The molecular size of MVHD-ACE was

far smaller than alkyd resin or drying oil, and the increase in MVHD-ACE would produce higher crosslinked structure in the dry film. Heat-bodied linseed oil was added to alkyd resin and MVHD-ACE in No. 5 and No. 6 to improve the flexibility of the dry film. The weight ratio of MVHD-ACE to the total resin in No. 5 and No. 6 corresponded to that of No. 2 and No. 3, respectively, and MVHD-ACE made it possible with or without the combination of heat-bodied linseed oil to prepare a high-solid paint and a superhigh-solid paint.

No. 1, which was formulated with only a conventional alkyd resin of high molecular weight, was outwardly brought to set to touch by evaporating the solvent, but the addition of MVHD-ACE had a tendency to retard it because of its low molecular weight. A slight increase in drying agent improved this tendency. Excess addition of MVHD-ACE in the total resin caused a highly crosslinked structure, and the impact strength was decreased, as shown in No. 4. The excess addition of MVHD-ACE also gave very faintly, yellowish-white color to No. 3, No. 4, and No. 6 in comparison with No. 1. These troubles were eliminated by adjusting the weight ratio of MVHD-ACE in the total resin to

TABLE III
Compatibilities of Alkyd Resins with MVHD-ACE

| Alkyd type and commercial name | Oil length | Phthalic acid content | Compatibility at 5:5 by weight | Manufacturer ^a |
|--|------------|-----------------------|--------------------------------|---------------------------|
| Mod. with soybean oil | | | | |
| Phthalkyde 235-50 | 35 | — | good | H |
| Becksol 1331 | 57 | 31 | very good | D |
| Becksol P-470 | 65 | 24 | very good | D |
| Solid Becksol 96 | 65 | 24 | very good | D |
| Becksol P-296 | 65 | 30 | very good | D |
| Phthalkyde 265-100 | 65 | — | very good | H |
| Becksol OD-E-198 | — | 40 | fair | D |
| Mod. with safflower oil | | | | |
| Becksol J-557 | 51 | 30 | very good | D |
| Becksol OD-E-188 | 85 | — | good | D |
| Mod. with linseed oil | | | | |
| Super Becksol 1313 | 42 | 41 | fair | D |
| Super Becksol EL-8011 | 85 | — | very good | D |
| Mod. with palm oil | | | | |
| Super Becksol J-524 | 32 | 44 | bad | D |
| Mod. with castor oil | | | | |
| Phthalkyde 444-50 | 44 | — | bad | H |
| Mod. with linseed oil and phenol | | | | |
| Super Becksol 1341 | 28 | 27 | very good | D |
| Mod. with Linseed oil, China-wood oil and Phenol | | | | |
| Super Becksol | 52 | 18 | very good | D |
| Mod. with linseed oil, China-wood oil, dehydrated castor oil, and phenol | | | | |
| Super Becksol J-611 | 35 | 25 | very good | D |
| Water-soluble type | | | | |
| Watersol S-100-D | | | fair | D |
| Watersol S-102 | | | fair | D |

^a H, Hitachi Kasei Co.; D Dainipon Ink Co.

below 30%. It was not easy to obtain a superhigh-solid paint (total solid content was 95%) by a small addition of MVHD-ACE to a conventional alkyd resin of high molecular weight. Lowering the molecular weight of alkyd resin could reduce the viscosity of the paint and the solvent content, but retard drying time,

TABLE IV
Compatibilities of Various Resins with MVHD-ACE

| Resin | Commercial name | Compatibility at | | |
|---------------------------------|-----------------|--------------------|---------------|-------------------|
| | | 5:5 by weight | Manufacturer | |
| Butyrated urea and melamine | Beckroll | very good | Dainipon Ink | |
| | Beckamine J-820 | fair | Dainipon Ink | |
| | Melan 11 | very good | Hitachi Kasei | |
| | Melan 20 | fair | Hitachi Kasei | |
| Heat-setting PMMA | Melan 30 | fair | Hitachi Kasei | |
| | Hitaloid 2462A | bad | Hitachi Kasei | |
| | | bad | | |
| | | bad | | |
| Nitrocellulose epoxy | Epikoate 827 | fair | Shell | |
| | Epikoate 834 | slightly | Shell | |
| | Epikoate 1001 | bad | Shell | |
| Hardener of epoxy | Arakdite HY 951 | bad | Ciba-Geigy | |
| | Tohomaide 215X | good | Fuji Kasei | |
| | Tohomaide 238 | bad | Fuji Kasei | |
| | Tohomaide 2400 | very good | Fuji Kasei | |
| | Tohomaide 2500 | very good | Fuji Kasei | |
| | Tohomaide 5000 | bad | Fuji Kasei | |
| Urethane prepolymers | Desmodure L | bad | Bayer | |
| | Desmophen 800 | bad | Bayer | |
| | Hiprene P 305 | good | Mitsui Toatsu | |
| Urethane hardener | MOCA | very good (1:9) | Ihara Chem. | |
| | | very good | | |
| Toluidine isocyanate polyethers | ADK P 700 | very good | Asahi Denka | |
| | ADK P 1000 | very good | Asahi Denka | |
| | ADK P 2000 | very good | Asahi Denka | |
| | ADK T 300 | bad | Asahi Denka | |
| | ADK T 400 | fair | Asahi Denka | |
| | ADK T 700 | good | Asahi Denka | |
| | ADK T 1500 | very good | Asahi Denka | |
| | ADK T 4000 | good | Asahi Denka | |
| | | | | |
| Petroleum resins | | | | |
| | Aromatics | Petrosine 80 | good | Mitsui Petrochem. |
| | | Petrosine 100 | very good | Mitsui Petrochem. |
| | | Petrosine 120 | very good | Mitsui Petrochem. |
| | | Petrosine 130 | very good | Mitsui Petrochem. |
| | Aliphatics | Quintol B 1000L | very good | Nippon Geon |
| | | Quintone U 135 | very good | Nippon Geon |
| | Polybutadiene | Nisso PB 1000 | very good | Nippon Soda |
| | | Nisso PB 2000 | very good | Nippon Soda |
| | | Nisso PB 4000 | very good | Nippon Soda |
| Unsaturated polyester | Upika | bad | Toyobo | |
| Chlorinated rubbers | CR 20 | bad | Asahi Denka | |
| | CR 70 | bad | Asahi Denka | |

and a lowering of the physical properties of the dry film was unavoidable. Recently, a superlong oil-length alkyd resin of low molecular weight could be applied to a high-solid paint of 85% solid content by addition of some metallic alcoholate.⁹ As listed in Table VI, a small addition of MVHD-ACE reduced the solvent of this paint to 5%, and this superhigh-solid paint showed excellent properties similar to those of the general conventional paint.¹⁰

EXPERIMENTAL

Measurements

Viscosity of Organic Compound. An Ostwold-type viscometer was used to observe viscosity at 25°C.

Viscosity of Paint. A No. 4 Ford cup viscometer (JIS K-5402) was used to observe it. Paint was placed in a cup (50 mm diameter, 60 mm height) and the paint was made to fall through the hole (4 mm diameter) from the bottom to observe the falling time which, was related to the viscosity.

Spectroscopy. A Nippon Bunko 402G infrared spectrometer and a Varian A-60 NMR spectrometer were used in this study.

Amount of Absorbed Oxygen. In a 50-ml flask equipped with a magnetic stirrer was placed 10 g sample with Co naphthanate, and the Co atom of the naphthanate was adjusted to be 0.1 gram-atom to 1 mole of the sample. After

TABLE V
Basic Recipes of MVHD-ACE for Alkyd Paints with a High Molecular Weight Resin

| | 1 ^a | 2 | 3 | 4 | 5 | 6 |
|--|----------------|-------|-------|-------|-------|-------|
| MVHD-ACE in total resin, wt-% ^b | 0 | 20 | 40 | 60 | 20 | 40 |
| Materials, wt-% | | | | | | |
| TiO ₂ | 29.29 | 33.57 | 37.33 | 41.24 | 37.15 | 41.27 |
| ZnO | 3.53 | 4.03 | 4.49 | 4.99 | 4.46 | 4.97 |
| Solid alkyd resin ^c | 34.75 | 31.91 | 26.54 | 20.03 | 25.34 | 18.62 |
| Heat-bodied linseed oil | | | | | 9.96 | 11.05 |
| MVHD-ACE | | 7.85 | 17.74 | 28.88 | 8.69 | 19.28 |
| 9% Co naphthanate | 0.2 | 0.23 | 0.26 | 0.28 | 0.25 | 0.29 |
| 24% Pb naphthanate | 0.61 | 0.68 | 0.78 | 0.84 | 0.75 | 0.86 |
| MEK-Oxim | 0.10 | 0.12 | 0.13 | 0.15 | 0.13 | 0.15 |
| Total solid, wt-% | 67.57 | 77.36 | 86.10 | 95.14 | 85.60 | 95.19 |
| Ford cup viscosity, sec | 72 | 73 | 69 | 69 | 79 | 79 |
| Dry time 23°C, 75% R.H. | | | | | | |
| Set to touch, hr | 2.0 | 4.0 | 5.0 | 5.5 | 3.5 | 4.5 |
| Dry hand, hr | 5.5 | 7.0 | 7.5 | 8.5 | 5.5 | 7.0 |
| Physical properties of dry film after 1 week | | | | | | |
| Pencil hardness | HB | HB | HB | HB | 2B | 2B |
| Mandrel 2 mm | OK | OK | OK | OK | OK | OK |
| du Pont, 1/2' × 1 kg | 50 cm | 50 cm | 50 cm | 40 cm | 50 cm | 50 cm |
| after 2 weeks | 50 cm | 50 cm | 50 cm | 40 cm | 50 cm | 50 cm |
| Erichsen mm | 8.7 | 8.5 | 8.2 | 7.3 | 8.8 | 7.9 |
| after 2 weeks | 8.4 | 8.4 | 8.0 | 7.0 | 8.6 | 7.6 |
| Cross hatch test 1 mm × 1 mm, 100/100 | OK | OK | OK | OK | OK | OK |

^a Recipe number. ^b Total resin = solid alkyd + MVHD-ACE + linseed oil. ^c Trade name Becksol P 470-70 (Dainippon Ink Co. Ltd.).

the closed vessel was evacuated completely and filled with oxygen gas at -78°C , the amount of oxygen molecule absorbed into the stirred sample was observed by a connected gas buret at 30°C .

Samples

Unsaturated Fatty Acid Methyl Esters. Oleic acid methyl ester (OME), linoleic acid methyl ester (LNME), and linolenic acid methyl ester (LEME) were purchased from Tokyo Kasei Co. and used without further purification.

1,3,7-Octatriene (OT).³ 0.76 g (1.9×10^{-2} mole) NaOH and 3.37 g (1.2×10^{-2} mole) oleic acid were added to 350 ml water and the mixture was emulsified by vigorous stirring. In a 1-liter autoclave were placed the emulsified solution, 0.53 g (3×10^{-3} mole) PdCl_2 , 1.57 g (6×10^{-3} mole) of triphenylphosphine, and 162 g (3 moles) butadiene, and the reactor was heated at 85°C for 15 hr. The mixture was cooled to room temperature and the organic layer was separated from the aqueous solution. The product was distilled at 127°C to obtain 1,3,7-octatriene, and the conversion was 94% based on butadiene. The physical constants were consistent with those in the previous report.

1-Phenyl-1,4,9-decatriene (PDT).⁴ 0.52 g (1.42×10^{-3} mole) $\text{Ni}(\text{acac})_2$,

TABLE VI
High-Solid and Superhigh-Solid Alkyd Paints

| | 7 ^a | 8 | Remarks |
|---|----------------|---------|------------------------------------|
| Materials, wt % | | | |
| Rutile TiO | 33.30 | 33.30 | |
| Body agent | 8.33 | 8.33 | |
| Super oil-length alkyd resin | 43.37 | 34.70 | |
| MVHD-ACE | — | 8.67 | |
| Total solid, % | 85 | 95 | |
| Etomar viscosity (20°C), kU | 75 | 75 | |
| Dry time 20°C , 75% R.H. | | | |
| Set to touch, hr | 2.5 | 3.5 | |
| Dry hand, hr | 8.0 | 10.0 | dry film thickness 40μ |
| Recoatibility, μ | | | |
| After 16 hr | 200 | 200 | maximum recoatable |
| After 24 hr | 250 | 200 | wet film thickness |
| Nonsagging film thickness, μ | 200 | 150 | |
| Gloss initial stage | 85 | 85 | 60° specular gloss |
| Weather-O-meter 300 hr | 50 | 50 | 60° specular gloss |
| Water resistance | | | |
| 3 days | OK | OK | primer undercoat. |
| 7 days | OK | OK | |
| 14 days | OK | OK | |
| 10% NaCl | | | |
| 7 days | OK | OK | |
| 14 days | OK | OK | |
| Pencil hardness | 3B | B | After 1 week dried |
| Erichsen 7 mm | OK | OK | at 20°C , 75% R.H. |
| du Pont $1/2' \times 500$ g, cm | 50 | 50 | dry film thickness 40μ |
| Cross hatch test 1 mm \times 1 mm | 100/100 | 100/100 | |

^a Recipe number.

0.523 g (4.59×10^{-3} mole) AlEt_3 and 0.7 g (2.02×10^{-3} mole) of triphenyl phosphite were dissolved in 22 g (0.212 mole) styrene at room temperature under nitrogen atmosphere in a 100-ml flask equipped with a mechanical stirrer and an inlet tube. Gaseous butadiene (0.74 mole) was charge into the solution at 105° to 115°C for 4 hr. The fact that the pressure in the flask was reduced immediately by the addition of butadiene showed complete absorption. Methanol (8 g) was added to the mixture to stop the reaction and the mixture was cooled to room temperature. A fraction bp from 105° to $135^\circ\text{C}/2$ mm Hg was collected, and the yield was 24 g. A gas-chromatographic analysis showed that the fraction contained 5% 1-phenyl-1,4,8-decatriene with 95% PDT, but its curing property was studied without further purification.

1-Methyl-2-vinyl-4,6-heptadieneol-1 (MVHD-OH).⁵ In a 2-liter autoclave were placed 3.87 g (17.25×10^{-3} mole) of $\text{Pd}(\text{OAc})_2$, 4.52 g (17.25×10^{-3} mole) triphenylphosphine, 931.5 g (17.25 moles) butadiene, and 379.3 g (8.26 moles) acetaldehyde. The reaction was carried out at 40°C for 20 hr, and 1185 g of product was obtained after evaporating unreacted compounds. This product contained 4% 1,3,7-octatriene, 8.3% 2,5-divinyl-6-methyl-tetrahydropyrene, 73.8% MVHD-OH, and 14.8% high boiling point fraction according to gas-chromatographic analysis. A fraction bp 60° to $62.5^\circ\text{C}/2$ mm Hg was collected, and the yield was 890 g. 2,5-Divinyl-6-methyltetrahydropyrene was removed by distillation under vacuum after acetylation of this fraction for reasons of having the same molecular weight as MVHD-OH. The acetylated residue was hydrolyzed with NaOH and distilled under vacuum to obtain purified MVHD-OH. The physical constants were consistent with the previous report.

Bis(1-methyl-2-vinyl-4,6-heptadienyl Succinate. In a 500-ml flask equipped with a mechanical stirrer and a dropping funnel, 101.8 g (0.67 mole) MVHD-OH and 92.1 g (0.76 mole) dimethylaniline were dissolved in 100 ml dry benzene. An initial addition of succinyl chloride gave the mixture a dark-brown color with a vigorous exothermic reaction, and the mixture was cooled to about 0°C to continue the addition of 51.9 g (0.335 mole) succinyl chloride. The mixture was heated to 80°C for 3 hr and cooled to room temperature. The mixture was washed, first, twice with 200 ml water, then with 200 ml 10% H_2SO_4 , and finally with 200 ml water to remove unreacted dimethylaniline and its HCl salt. The organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to leave a dark residue, which was purified on a silica gel column eluting with *n*-hexane. The conversion was 91.8% based on MVHD-OH; n_D^{25} 1.4954, d_4^{15} 0.9775.

ANAL. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_4$: MW 386.5; C, 74.59; H, 8.85; O, 16.56. Found: MW (VPO) 364; C, 73.95; H, 8.88, O, 17.17.

1-Methyl-2-vinyl-4,6-heptadienyl 3,8-Nonadienoate. In a 1-liter autoclave were placed 0.294 g (1.31×10^{-3} mole) $\text{Pd}(\text{OAc})_2$, 1.362 g (5.198×10^{-3} mole) triphenylphosphine, and 55 g (0.362 mole) MVHD-OH. Liquid butadiene (110 ml) and CO gas (initial pressure 50 kg/cm^2) were charged into the reactor, and the reaction was carried out at 100°C . The pressure was raised to 71 kg/cm^2 and finally reduced to 57.5 kg/cm^2 after 16 hr. The reactor was cooled to room temperature to remove unreacted butadiene and CO . This product was distilled

under vacuum to collect a fraction bp from 133° to 133.5°C at 2 mm Hg, and the conversion was 90.3% based on MVHD-OH; n_D^{25} 1.480, d_4^{18} 0.914.

ANAL. Calcd for $C_{19}H_{28}O_2$: MW 288; C, 76.85; H, 9.84; O, 13.31. Found: MW (VPO) 274; C, 79.12; H, 9.78; O, 11.09.

1,1-Bis(1'-methyl-2'-vinyl-4',6'-heptadienoxy)ethane. In a 100-ml flask equipped with a mechanical stirrer were placed 5 g (0.045 mole) anhydrous $CaCl_2$ and 20.4 g (0.134 mole) MVHD-OH. A uniform dispersion was prepared under nitrogen atmosphere by vigorous stirring at about 5°C, and 4.4 g (0.1 mole) acetaldehyde was added to the dispersion. The temperature was raised to 15°C, and the reaction was continued for 4 hr. $CaCl_2$ was separated by filtration and washed with *n*-pentane which was mixed with the filtrate. A fraction bp from 144° to 148°C at 2 mm Hg was collected by vacuum distillation, and the conversion was 92% based on MVHD-OH; n_D^{25} 1.4908, d_4^{15} 0.9025.

ANAL. Calcd for $C_{22}H_{34}O_2$: HW 380.5; C, 79.94; H, 10.38; O, 9.68. Found: MW(VPO) 349; C, 79.74; H, 10.49; O, 9.77.

The authors are greatly indebted to Drs. T. Tomiyama, S. Kodama, and T. Watanabe of Kansai Paint Co. Ltd. for helpful discussions and interesting data.

References

1. Los Angeles County Rule 66 Revise II Nov. 2, 1972, *Fed. Reg.*; **36** (No 67), April 7, 1971.
2. Y. Inoue, *Paint and High Polymer*, Seibundoshinkosha, Tokyo, 1964, p. 133.
3. S. Takahashi, T. Shibano, and N. Hagiwara, *Bull. Chem. Soc. Jpn.*, **41**, 454 (1968); S. Enomoto et al., Japan. Pats. 51-23202 and 51-23203 (1976).
4. P. Heimbach, P. W. Jolly, and G. Wilk, *Adv. Organometal. Chem.*, **8**, 29 (1970).
5. R. M. Manyik, W. E. Walker, K. E. Atkins, and E. S. Hammack, *Tetrahedron Lett.*, 3813 (1970).
6. S. Enomoto et al., Jpn. Pat. 51-34109 (1976).
7. W. Keim and H. Chung, *J. Org. Chem.*, **37**, 947 (1972).
8. H. Dannenbarg, *S.P.E. J.*, **15**, 10 (1952).
9. M. Kawamura et al. Jpn. Pat 51-8323 (1976).
10. T. Watanabe, Meeting of Paint and Print ink held in Tokyo, June 9, 1976.

Received July 30, 1976

Revised November 5, 1976