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F & F Dept. R & D Division.
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DuPont de Nemours, E.I. & Co. F&F DEPTMENT.
R&D DIVISION. MARSHALL LA.

PROPOSED PUBLICATION FROM THE FABRICS & FINISHES DEPARTMENT

MODERN DEVELOPMENTS IN ORGANIC COATING TECHNOLOGY

BY SEYMORE HOCHBERG

We submit for your information and comment a proposed paper on Modern Developments in Organic Coating Technology.

This paper has been prepared for oral presentation at a meeting on Frontiers of Science in Industry in Israel during the week of March 10, 1974. The paper will not be published. There is no proprietary information involved; no patent applications are contemplated on the material.

We will be pleased to have any comments or suggestions that you care to make. Unless we hear from you by March 4 we will assume you have no objections.

R. W. LAURRELL
R&D Manager

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The bulk of surface coatings are used for the protection and decoration of substrates. Such specialties as fire-resistant coatings, insulation for wires, and coatings for magnet tape are somewhat smaller in volume but not insignificant.

For many years the major objectives of Research and Development have been the improvement of quality, reduction in cost, new appearance effects, and enlargement of the market by extension to substrates not currently coated.

While the traditional objectives are always kept in mind during continuing research and development activities, they appear now to have taken a secondary position relative to a response to certain emergencies which may turn out to be of long duration. The emergency situations are the social drives and the consequent laws regarding toxic hazards, the problem of water and air-pollution, the recent and anticipated shortages of fluid fuels, and the shortage of chemical products derived from petroleum.

STATE OF THE ART WITH RESPECT TO:

A. QUALITY

1. Outdoor Durability - The quality of automotive finishes is such that ten-year durability is readily achieved. The coatings can last longer than the automobiles themselves, provided one is content with a wide but limited color range. House paints properly applied over durable substrates have similar long life compared with the substrates. Coatings for aluminum and steel strip carry long term warranties against fading and peeling, and they are expected to survive. There is little incentive for improvement of durability to exposure. Incentives for cost reduction always exist, however.

2. High-Temperature Resistance-Coatings for wire are available in a series of classes in accordance with temperatures of use. Continuous use of over 220°C with good mechanical cut-through properties can be obtained with aromatic polyimides. At this temperature the usual metals fail by oxidation. No incentive exists for improvements above the quality of aromatic polyimides.

3. Resistance to Household Deteriorating Influence-Home appliances can be coated with a variety of products which will not fail in many years of service. There is not incentive to improve color-stability, staining, resistance to grease, or resistance to soap and hot water for any of the home appliances now used.

4. Coatings for Pots and Pans-Coatings of polytetrafluoroethylene or kitchenware yield the best food release we know how to obtain. While substantial improvements can be envisaged over the polytetrafluoroethylene in scratch and stain resistance, there appears to be little hope of producing the hard, yet formable, stain-repellent material needed.

5. Maintenance Coatings-Coatings for tanks, bridges, and other heavy steel construction can use some improvement. At present, the chief weakness of such finishes would appear to be related to the preparation of the surface for painting. Painting over rust or loose surfaces is the cause of early failure no matter what is put on top.

Improvements in quality over traditional materials for these markets is apt to be small, it would be different to demonstrate and important competitively perhaps in isolated instances but not important on a social basis. Incentives exist for reductions of cost - particularly for less vigorious exposures.

B. APPEARANCE:

A wide range of colored pigments and their metallic modifications with aluminum pigment make possible the wide variety of automotive colors. In addition, various textures are possible through the use of large pigment particles, coarse incompatible pigment dispersions of contrasting colors and mechanical methods of introducing texture. High degrees of iridescence, as with liquid cholesteric crystals, are not yet on a practical basis, but might capture a significant market. The iridescent, plate-like, pigment "Afflair" has some of the qualities of aluminum but it is not as bright.

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The need for painting soft substances in resulting in a flurry of activity. The soft substrates are plastic and rubbery materials now required in automobiles. Current materials do not perform satisfactorily over the required temperature range or are not sufficiently durable.

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1. Computers are being used to predict the course of polymerizations and to make adjustments in processing in order to tailor-make polymers with desired properties. Not only can the molecular weight and copolymer composition be predicted, but the fine-structure of the polymer, represented by sequences in a given polymer chain, can be engineered.

2. Computers are being used to control color and to guide shading operations to yield matches of high quality with a minimum number of trial additions. Kubelka-Munk theory is used.

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The response of R&D has been to concentrate on exempt type finishes i.e., less than 20% solvent (photochemically-inactive) and to convert the non-conforming current types of solvent mixtures to conforming ones by substitution of relatively innocuous for relatively obnoxious solvents. The exempt-type finishes are the so-called high-solids finishes, the aqueous finishes, and powder finishes.

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Enamels: Low molecular weight polymers which are crosslinked during baking are made at the lowest practical molecular weight and diluted with a minimum of solvent of conforming (Rule 66) types. Pigments are dispersed in the solutions. The quantity of solvent can be reduced and can be limited to aliphatic hydrocarbons if the polymers are stabilized against flocculation in hydrocarbon. The finishes usually comprise low molecular weight hydroxyl-terminated polyesters mixed with low molecular weight melamine-formaldehyde or capped diisocyanates or polyisocyanates.

Lacquers: Relatively high molecular weight polymers are dispersed in predominately aliphatic hydrocarbons using graft copolymers as dispersing agents. Pigments are dispersed separately. On evaporation of solvent the polymer particles coalesce.

Another type of high solids finish contains high-boiling solvents which are converted to polymeric materials after application to a substrate. The mechanism of conversion is usually exposure to ultra-violet light or high-speed (ionizing) electrons.

The organic-solvent based finishes are applied by spray, automatic or manual, can be sprayed and deposited electrostatically, and can be applied by rollers.

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Lacquers: Ammonium salts of carboxyl-terminated polymers, usually with small amounts of auxiliary solvents, are applied by spray from relatively dilute aqueous solution. The films lose water-sensitivity on evaporation of ammonia. The polymer can be used in latex from or as micellar solutions.

Enamels: Somewhat more concentrated dispersions of lower molecular weight, hydroxylated polymers are combined with melamine resins and pigment dispersions. These convert on heating to insoluble crosslinked form. Other drying mechanisms might be used.

Aqueous finishes can be applied by conventional spray and dip methods. Special electrocoating methods have been developed.

ELECTROCOATING:

Anodic Deposition

A dilute dispersion of salts of carboxylated polymers is mixed with a crosslinking agent and pigments. The viscosity is barely greater than that of water. The passage of electric current through the bath of the substrate, which is the anode, deposits a viscous mixture of vehicle and pigment on the substrate. Coalescence of the polymer produces a film of low conductivity which limits the thickness of the deposit. The substrate is drawn from the bath with only a minor amount of entrained, uncoalesced paint. This is rinsed off. The deposit which is left on the substrate is baked to convert it to insoluble form.

The electromotive force for electrodeposition is about 100-500 volts and the e.m.f. is much higher than that required for electrolytic reactions. It results in electrophoresis of the negatively charged particles toward the anode. At the anode, acids are produced through electrolysis of water, and metals are dissolved from the electrode. The acids and the metals destabilize the mixture and a viscous, slimy mass is deposited on the anode. If the acidified polymer can coalesce (a Tg bath temp) it will form a coating of low conductivity and limit the thickness of the applied coating. When the deposition stops the e.m.f. across the coating will equal the applied e.m.f. and the potential gradient will be 10,000 to 100,000 volts/inch.

The acidified deposited polymer is initially laden with water, but the flow of current causes some of the water to leave by a process of electroendosmosis, producing a denser deposit than that produced by acidification alone.

Oxygen liberated at the anode forms bubbles in the deposit. The deposits are therefore initially rough. A smooth system can be obtained only if the deposited film is sufficiently fluid to smooth out by forces of surface tension. Under these conditions, edges, which are preferred positions for the initial deposit, may be left uncovered.

Cathodic Deposition

The substrate to be coated is made the cathode. The polymer is usually in the form of polymeric amine, solubilized as a salt.

POWDER COATINGS AND THEIR APPLICATION:

Powder coatings are made of particles of 10-30 microns diameter each of which contains the pigment and the binder. The binder will usually comprise a low-molecular-weight, brittle, resin mixture which is stable enough at room temperature but which melts and reacts at oven temperatures to produce a high-molecular weight, tough polymer as required. The manufacture of powders requires the development of manufacturing techniques to yield suitable size, suitable color, and suitable flow properties and reactivity in the oven. The finished coating must also meet the service requirements. Epoxy resins and hydroxyl-containing acrylic resins or hydroxylated polyesters are used with appropriate reactive crosslinking agents.

Powder coatings can be applied to a hot object by dipping it into a fluidized bed of the powder. The powder melts and sticks to the surface. The thickness depends on the local heat capacity and temperature of the object being coated. Thick coatings are readily applied by fluidized bed techniques.

Thin coatings are applied by spraying the powder, charging it electrically, and attracting it to the surface by electrostatic forces. As the powder collects, its charged particles tend to reduce the electric field, and this limits the thickness. The conductivity of powders determines the film thickness and must be controlled between certain limits.

The application of powders for protection alone is done fairly easily, but decorative applications are difficult for a variety of reasons. Once coated and coalesced a surface can be difficult to recoat by electrostatic deposition.

Part of the problem with obtaining good appearances with powders is that the density of the applied powder is low, containing much air. The coalescence of the particles causes shrinkage - not necessarily all away from the surface. Furthermore, gases are often liberated by cross-linking reactions. While smoothing by surface tension proceeds, the polymer hardens, Smoothness equivalent to that of solution applied coatings, therefore, is difficult to achieve.

Powders are also available for application as dispersions in water. Such powders can conceivably yield denser films.

IMPACT OF THE NEW AIR POLLUTION REGULATIONS ON FINISHES SALES:

Within the last ten years the pattern of industrial finishes sales has changed significantly away from solvent-thinned paints. The regulations will accelerate the change. In 1975, while solvent-thinned paints will probably still represent the majority of the industrial paint sold, the sales of alternates will represent a substantial fraction. (See Figure 1, 2, 3, quoted from Industrial Finishing and Surface Coating, pp. 14, 15 Aug. 1973).

Sales of paint to ultimate consumers will be affected less by the air-pollution regulations because the more obnoxious solvents were eliminated from these paints years ago.

RESPONSE OF R&D TO POWER SHORTAGE:

The shortage of power makes it necessary to reduce baking temperatures. Usually in one-package systems when reactivities are high at low baking temperatures, stability in storage is poor. The conventional air-drying oil-based systems are in reality two package systems of which one package is air. Moisture-cure (making use of atmospheric water-vapor) of isocyanate terminated polymers, ultra-violet radiation cure, and electron-beam irradiation of vinyl monomers act like two-package systems. They are stable at room temperature, yet react rapidly under certain conditions at room temperature.

SPECIAL PROBLEMS

WITH AQUEOUS FINISHES:

1. Reactivity of aluminum flake.
2. Spraying problems with electrostatic equipment.
3. Humidity control in drying.
4. Heat requirement for evaporation of water.
5. Corrosion of equipment.
6. Salt-content.
7. Hydrophilic even when dry.
8. Cross-linking mechanisms need improvement.

WITH ELECTROCOATING:

1. Investment in equipment.
2. Bath composition changes - Pigment, Solvents, Binder, Salts, Acid-base balance.
3. Control of bath composition not simple - Flushed cathodes (or anodes), reverse osmosis.
4. Contamination with materials dragged in by the substrate.
5. Anodic electrocoating dissolves metal from the electrodes, including metal pretreatments, yielding color and poorer pretreatment surface. This is not true of cathodic deposition.
6. Gases form at the substrate.
7. Washings must be recovered (reverse osmosis).

WITH POWDER COATINGS:

1. Clean-up between colors is expensive.
2. Metallic colors lack brightness.
3. Electrostatic fields do not enter cavities.
4. Recoating can be difficult.

WITH ULTRA VIOLET CURE:

1. Line of sight cure.
2. Pigments, oxygen, exudates from substrates interfere with polymerization.
3. Ozone, heat.

WITH ELECTRON-BEAM CURE:

1. Pigments, oxygen, exudates from substrates interfere.
2. Large capital investment.
3. Dangerous X-rays produced.

FIGURE I

U. S. PAINT INDUSTRY MARKET SIZE - MILLION GALLONS

	1966	1968	1970	1971	1972	1975*	1980*
Industrial	421	424	399	443	485	525	630
Trade Sales	416	419	428	431	465	515	595
Total	837	843	827	874	950	1040	1225

*ESTIMATES

C. H. Kline & Co. Marketing Guide to the Paint Industry.

Industrial Finishing and Surface Coatings (Aug. 1973) pp. 14, 15

FIGURE II

U. S. PAINT INDUSTRY MARKET SIZE - MILLION GALLONS

INDUSTRIAL SALES

	1966	1968	1970	1972	1975*
Solvent Thinned					
Air Dry or Force Dry	131	128	123	103	98
Bake	278	262	234	296	227
Water Thinned					
Air Dry or Force Dry	3	5	5	8	18
Bake	5.5	20	34	73	162
Powder					
Epoxy	1	1	1	1.5	5.0
Polyester				0.2	1.0
Other	2.5	3	3	3.3	6.0

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FIGURE III

U. S. TRADE SALES MARKET

	1966	1968	1970	1972	1975*
Solvent Thinned					
Interior	74	60	58	45	9
Exterior	92	75	62	53	28
Water Thinned					
Interior	136	159	170	212	223
Exterior	51	66	72	91	115
Other Solvent Thinned	63	60	61	64	40
Total	416	419	428	465	515

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Powder coatings are made of particles of 10-30 microns diameter each of which contains the pigment and the binder. The binder will usually comprise a low-molecular-weight, brittle, resin mixture which is stable enough at room temperature but which melts and reacts at oven temperatures to produce a high-molecular weight, tough polymer as required. The manufacture of powders requires the development of manufacturing techniques to yield suitable size, suitable color, and suitable flow properties and reactivity in the oven. The finished coating must also meet the service requirements. Epoxy resins and hydroxyl-containing acrylic resins or hydroxylated polyesters are used with appropriate reactive crosslinking agents.

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4. Heat requirement for evaporation of water.
5. Corrosion of equipment.
6. Salt-content.
7. Hydrophilic even when dry.
8. Cross-linking mechanisms need improvement.

WITH ELECTROCOATING:

1. Investment in equipment.
2. Bath composition changes - Pigment, Solvents, Binder, Salts, Acid-base balance.
3. Control of bath composition not simple - Flushed cathodes (or anodes), reverse osmosis.
4. Contamination with materials dragged in by the substrate.
5. Anodic electrocoating dissolves metal from the electrodes, including metal pretreatments, yielding color and poorer pretreatment surface. This is not true of cathodic deposition.
6. Gases form at the substrate.
7. Washings must be recovered (reverse osmosis).

WITH POWDER COATINGS:

1. Clean-up between colors is expensive.
2. Metallic colors lack brightness.
3. Electrostatic fields do not enter cavities.
4. Recoating can be difficult.

WITH ULTRA VIOLET CURE:

1. Line of sight cure.
2. Pigments, oxygen, exudates from substrates interfere with polymerization.
3. Ozone, heat.

WITH ELECTRON-BEAM CURE:

1. Pigments, oxygen, exudates from substrates interfere.
2. Large capital investment.
3. Dangerous X-rays produced.

FIGURE I

U. S. PAINT INDUSTRY MARKET SIZE - MILLION GALLONS

	1966	1968	1970	1971	1972	1975*	1980*
Industrial	421	424	399	443	485	525	630
Trade Sales	416	419	428	431	465	515	595
Total	837	843	827	874	950	1040	1225

*ESTIMATES

C. H. Kline & Co. Marketing Guide to the Paint Industry.

Industrial Finishing and Surface Coatings (Aug. 1973) pp. 14, 15

FIGURE II

U. S. PAINT INDUSTRY MARKET SIZE - MILLION GALLONS

INDUSTRIAL SALES

	1966	1968	1970	1972	1975*
Solvent Thinned					
Air Dry or Force Dry	131	128	123	103	98
Bake	278	262	234	296	227
Water Thinned					
Air Dry or Force Dry	3	5	5	8	18
Bake	5.5	20	34	73	162
Powder					
Epoxy	1	1	1	1.5	5.0
Polyester				0.2	1.0
Other	2.5	3	3	3.3	6.0

*ESTIMATE

C. H. Kline & Co. Marketing Guide to the Paint Industry

Industrial Finishing and Surface Coating (Aug. 1973) pp. 14, 15

FIGURE III

U. S. TRADE SALES MARKET

	1966	1968	1970	1972	1975*
Solvent Thinned					
Interior	74	60	58	45	9
Exterior	92	75	62	53	28
Water Thinned					
Interior	136	159	170	212	223
Exterior	51	66	72	91	115
Other Solvent Thinned	63	60	61	64	40
Total	416	419	428	465	515

*ESTIMATE

C. H. Kline & Co. Guide to the Paint Industry

Industrial Finishing and Surface Coatings (Aug. 1973) pp. 14, 15