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Marshall R&D Laboratory
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The needs of the finishes industry have been successfully met by solvent borne coatings. We are faced, today, with the possibility that the use (or at least the emission into the atmosphere) of solvents will be severely proscribed. This memorandum tries to examine the various known solvent free approaches to industrial finishing and to discuss their suitability for specific end uses at this time.

I hope that this will help Research and Marketing Management to choose the most suitable alternatives and develop R&D programs and Marketing strategies for the future health of the Department.

Werner S. Zimmt
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ALTERNATE APPROACHES

TO

POLLUTION FREE FINISHES

JUNE 18, 1971

WERNER S. ZIMMT

ALTERNATE APPROACHES TO POLLUTION FREE FINISHES

INTRODUCTION:

The current trend in air pollution control regulations suggests the probability that in the not too distant future we will have to supply our customers either with technology to recover solvents economically, or with finishes that add little or no contributions to air pollution. Several major finishes users have already indicated that they expect their suppliers to develop solvent free or non-polluting finishes in the next few years.

A number of different approaches to coatings containing little or no organic solvents are known and have been in commercial use for some time. Most of these have limitations that restrict their utility to specific situations where they offer unique solutions or advantages. These limitations together with the acceptability of existing solvent-borne systems have prevented the expansion of solvent free finishes into wider areas of coating technology.

It is the purpose of this report to analyze the various approaches to solvent free coatings, to consider their advantages and disadvantages with respect to various end use requirements, to determine in what areas they might profitably be used, and to try to suggest what accomplishments are needed to allow them to succeed.

In order to reduce this task to manageable proportions certain simplifying assumptions will be made:

- In a given industry or segment of an industry similar conditions and requirements prevail, so that one approach can be used by most or all customers in that industry.

- The conditions and requirements that prevail today are a reasonable guide to what can be expected at the time that pollution free finishes come into use.

- Our customers will be willing to make reasonable changes in their processes and equipment in order to comply with air pollution regulations and to stay in business. I would not expect airplane manufacturers to install baking ovens, or coil coaters to run lines at 10 ft./minute, but the former may have to use two headed spray guns and control humidity in the spraying areas, and the latter may have to use different materials in their pickup rolls to prevent solvent swelling.

I will try to discuss the various broad classes of pollution free coatings, what is known about them, what properties can be expected from them, and what their conditions of use are likely to be. I will then try to estimate how suitable they may be for specific end uses, and finally I hope to be able to point out what work will need to be done to develop practical products. Legislation and technology are changing rapidly, but this discussion is as current as I can make it.

There are many reasons for using organic solvents in coatings, the most important one being the control of the rheology of the paint and ease of obtaining a continuous, well coalesced film on the substrate.[1] Over the years solvents with a wide range of evaporation rates and solvency have become commercially available, allowing the formulator to choose combinations that suit the requirements of his particular systems. Fast evaporating organic solvents are especially effective in providing for a rapid increase in viscosity at the point of application. This property is essential for spray application since a low viscosity is necessary to permit rapid flow and good atomization from the spray gun, but a much higher viscosity is necessary to keep the paint from running off non-horizontal surfaces once it reaches the area that is being coated. Organic solvent systems also allow adjustment to changes in ambient temperatures by using solvents with different evaporation rate,and are generally not sensitive to the relative humidity.

Solvent borne coatings can be applied with a wide variety of devices, since the paint can be adapted to the requirements of the equipment by changes in the solvent composition.

The following criteria will be considered in discussing solvent free systems:

Flow Control (Rheology)
Film Formation (Coalescence)
Sensitivity to ambient conditions
Application equipment
Possible pollution problems

There are several distinct approaches to finishes that emit no or small quantities organic solvents during application and film formation. These include: lamination of a preformed film; using water as a solvent or dispersing medium; using a solvent free liquid composition that forms dry films,and applying a powder that coalesces to a continuous film on the substrate.

<u>Lamination of Films</u>

The lamination of preformed film is an excellent technique as long as the substrate is a flat surface, or one that is curved only in one direction. However, the coating film must be sufficiently strong to allow handling when unsupported, which is not the case with many paint films used today.

Its major application has been in coating films or metal coils, such as aluminum, to be shaped at a later time. It requires a suitable adhesive and is best used on a continuous process operation. Since the film is preformed there are no problems with coalescence or rheology during the application process and ambient conditions affect the process only to the extent that they can affect the adhesive. If the latter is a solution some pollution potential exists, but, because the volume is usually much smaller, only on a reduced scale. Waterborne adhesives would eliminate this too. The equipment used for film lamination is highly specialized and represents a major investment.

As far as F&F is concerned, free films seem to offer little opportunity, since we do not produce or sell them. Film Department produces and sells Tedlar® polyvinyl fluoride film as a metal coating. F&F manufactures and sells a solution adhesive, but at present this represents a small volume item.

Water Based Coatings

Many efforts have been made to introduce water borne finishes. They have been highly successful in the consumer paint area, where the ease of application, the ease of clean-up and the rapid dry and low odor of latex paints have essentially preempted the house and wall paint market for water borne finishes. The binders used for this end are soft (for low temperature coalescence), slightly hydrophyllic (for moisture transmission) and of very high molecular weight. Small quantities of high boiling water soluble organic solvents are used to improve application properties.[2]

Entry into the industrial market has proven to be much more difficult. The major advantages foreseen for water borne finishes are low air pollution potential, lower cost, reduced fire hazard and the expectation that existing equipment can be used for their application.

The problems encountered have been due to the need for water sensitive dispersants or functional groups, uneven distribution of polymer and pigment phases in the final film and the fact that ambient conditions affect application properties much more strongly than they do solvent borne coatings. Furthermore, in solvent borne coatings the solvent can be adjusted to suit changes in ambient conditions, which is not possible in systems using only water.[3] As a result of these difficulties most industrial applications have developed for end uses that do not require high standards of appearance or performance.

Considerable progress has been made in overcoming these known deficiencies and it is quite probable that the current emphasis on reduction of solvent emissions will accelerate the rate of progress.

Currently water dispersed paints are entering the industrial and automotive market in large volume for electrodeposition applications. This is their first major penetration.

However, even in this application some solvents are used in many, but not all formulations. The resin, when deposited is at 60% to 85% solids, and an appreciable fraction of the volatiles can be organic solvents.[4] These are evaporated during the baking cycles and may have to be recovered or destroyed if a total ban on emissions is enacted. Los Angeles is contemplating a change that would permit the use of up to 20% by volume of non-photochemically reactive solvents in water without any control.

The role of the organic solvent in electrophoretic deposition has not been fully explained, but the solvent is known to affect coalescence, film thickness and also appearance. If the use of volatile solvents must be restricted, substitution of a non-volatile reactive liquid should be considered.[5] For instance, a diglycidyl monomer, that can react with acids group or a diacrylate than can cross-link a maleic polyester during cure could be substituted for part or all of the solvents. Such approaches should be given serious consideration in any long range scouting.

Spray or flow application of water based paints is made difficult by the dependence of the evaporation of water on ambient temperatures and humidity. This affects the necessary increase in viscosity, and frequently leads to popping and blistering of the final film.[3,6] Hot spraying may be of some help, and high air pressures are known to help.

C. Victorius recently showed that part of these problems can be overcome by adding a viscosity increasing material to the spray. In his experiments he obtained the desired viscosity increase in a water borne coating by adding a stream of ammonia to a carboxylic acid latex; similarly the addition of CO_2 to an amine containing dispersion would result in an increase in viscosity. This approach should be much less sensitive to ambient conditions than trying to control the removal of part of the water during application.

From the increasing number of publications it is apparent that work on water borne coatings is proceeding in many locations. The technology is extensive (J. C. Fang's Report R-59-35), and the principles are well known.[7] What has been missing is the incentive to the paint manufacturers to do the work necessary to overcome the known defects, and to the user to test and introduce new developments. The pollution crisis can be expected to furnish this incentive.

In addition to developing better vehicles that are free of all solvents further work needs to be done to understand the various rheological problems that lead to popping and also the pigmentation difficulties. For possible automotive topcoat uses, the development of a water stable glamor flake would be essential.

The large scale manufacture of water borne coatings will also lead to some waste disposal problems, since plant effluents will not be allowed to enter rivers or sewers without purification. Currently used biocides, based on phenyl mercury acylates, will have to be replaced by non-mercurials.

Powder Coating

Powder coatings are beginning to generate considerable interest in the coating industry. Fluidized bed coating, which involved dipping a hot object into a fluidized bed of fusible powder has been used many years.[8] However, this technique generally leads to coatings 10 to 50 mils thick. With the advent of electrostatic powder application 2-4 mil thick coatings became possible on conducting substrates.[9] The operation of this process depends on directing a charged powder at a grounded, conducting surface. Theoretically, the powder retains its charge on the work surfaces, and once the surface is covered no more powder deposits. Thus, self limiting films are possible, although not always found in practice.

Powder coatings eliminate the need for any liquid solvents or carriers during application. No evaporation or increase in viscosity is required. As long as the electrostatically attached powder is not disturbed mechanically, it will stay on the work for a reasonable length of time, so that it can be conveyed to an oven for fusion and crosslinking, if this is desired.

While this process is simple in theory in practice it is less so. The resistivity of the powder must be in a specific range. The particle size of the powder affects the process and the final product but no agreement exists on optimum size or distribution.[13] Provisions must be made for complete coalescence of the powder, which means it must be able to flow at a practical temperature.

The major raw materials for painting by thin film powder applications up to the present have been epoxy powders.[8] Coatings based on polyesters or acrylic polymers[10] are just now being introduced. All of the currently available systems are enamels in the sense that they crosslink during the fusion process.

Non cross-linked powders have been used in the older fluidized bed technique. These most frequently were polyolefins or polyamides; some PVC and CAB powders were also used.[8]

In addition to electrostatic spraying other techniques are under consideration. Flame spraying, where powder is fed into a flame so that it melts and arrives at the work in the molten states is probably the most promising, since it is claimed to be able to deliver large enough quantities of polymer to be economically feasible.[9] Plasma spraying can deposit metals as well as polymers, but its rate of delivery of powder to the surface is too low to be practical for industrial use, except in unusual cases.[11]

The coalescence of the electrostatically deposited powders is accomplished by heating the coated surface beyond the melting point of the powders. The use of low molecular weight materials, such as the epoxies, ensures that the melt is sufficiently low in viscosity to flow and coalesce into a continuous film free of macroscopic voids. The cross-linking reaction must be controlled so that coalescence occurs before cross-linking. When higher molecular weight polymers are used the problems of flow and coalescence become more critical, especially as viscosity above some critical molecular weight depends on the 3.4 power of the molecular weight.[12]

Experience with epoxy powders has shown that their use is economically feasible only when overspray can be recovered and reused, but with proper recovery >90% utilization has been claimed.[13] Because of non-uniform deposition, both particle size as well as pigment to binder ratio can be different in the overspray than in the original material, so that recycling may be complicated.[23] If different colors are sprayed in the same equipment the requirement for overspray recovery causes further difficulties in recycling the materials that still have not been resolved. If only 2 or 3 colors are used and volume is sufficient, then one booth for each color is feasible.

The major problems associated with the preparation of powder coatings are those dealing with dispersion of pigments and color control. The type of shading process that is normally used in liquid finishes is not suitable for powders. The color in powder coatings is normally incorporated by sequence of a dry blending, melting, extrusion and grinding. If the resultant color match is poor, the entire process would have to be repeated. Aside from the expense of such a procedure, the thermosetting powders have limited stability of the melt temperature, so that reprocessing could lead to partial gelation.

If the polymer powder is simply mixed with the pigment there is a tendency for the two to separate on storage or application because of the differences in density. This too makes color control difficult. Currently there is no practical method known of shading powder polymers to the degree of color tolerances normally expected in paints.

Aside from the pigmentation difficulties the preparation of powders per se represents technical problems. The shape as well as the size is important.[13] Rough, jagged edges can lead to poor flow and make powders difficult to fluidize or blend. The preparation of powders from high molecular weight, tough polymers by grinding at ordinary temperatures is difficult. Considerable quantities of heat are developed that soften the polymers and prevent adequate, effective dimunition. This can often be overcome by grinding at low temperatures, but at an increase in cost. Screening and recycling facilities will have to be available. Mixes will have to be reprocessed.

Another approach is to prepare polymers in the final particle size directly, for example by suspension polymerization. This has been done on a small scale and would be a more desirable approach if a suitable process to give the desired particle size and distribution is available. It may be possible to disperse pigments in the monomers before polymerization, in which case better color control is probable.[14]

Much of the early work on powder coating in F&F has been done by converting solution paints into powders, mostly by spray drying. This method allows all formulation and shading operations to be completed before converting the solution to a powder but, in terms of pollution control, it transfers the problem of solvent removal from the paint user to the paint manufacturer.[14] A possible alternative might be to disperse the final composition in a non-solvent for the paint that will extract the solvents and leave dry particles behind. This could be water or some other liquid. The active solvent can then be recovered and reused, while not creating any air pollution problems. This approach, if successful would constitute a closed system as far as the solvent is concerned. However, its feasibility must still be proven. Another possibility is to prepare the final composition in aqueous emulsion or dispersion and spray dry without the need for solvent recovery.

Solvent-Free Liquid Coatings

Solvent free liquids are, among the oldest paint binders known. Linseed oil has been in use since the Middle Ages, and other oils also have a long history of use. These material generally suffer from slow drying, poor durability and lack of control of application properties. They were displaced when higher molecular weight materials, such as cellulosics and alkyds, became available. The high viscosity of these substances could be controlled by use of volatile solvents, which led to the introduction of spray application. Recent efforts to develop solvent free, rapid curing coatings have been successful from the synthetic viewpoint. Low viscosity air drying systems have been developed, based on allyl ether substituted acrylic monomers,[16] or polyfunctional 2-vinyl dioxolanes,[17] or on the esters of polybasic unsaturated acids with 3,4 dihydro 2-H-pyran-2-methanol.[18] These all can be air dried or baked to give finishes with many desirable properties.

In practice they failed, in part because their application properties could not be controlled in a practical monomer. This is one of the major problems of solvent free finishes.[22]

Several types of solvent free coatings are in some limited use. Polymer-monomer syrups can be used for finishes. These contain volatile monomers that are in many ways more objectionable than most solvents, partly because of inherent toxicity, and partly because of air pollution potential. Most of these materials also do not cure well in the presence of air and hence need waxor some other surface covering to prevent or reduce monomer loss and air inhibition.[19] These surface coverings must then be removed, which causes processing difficulties.

As mentioned natural oils or modifications can be used in solvent free finishes, generally for brushing products.

Some effort has been made to use dual delivery systems to apply rapidly reacting two component liquids which will polymerize to high molecular weight crosslinked coatings.

This approach, although only moderately successful up to now, may become more interesting as the use of solvents becomes more restricted.

Another approach to solvent free coating has been to cure flat or cylindrically shaped articles with high energy radiation. In the case of flat substrates the liquid coating is rolled onto the surface and the panel is then exposed to radiation to affect a rapid cure. Since the finish is not sprayed, viscous materials can be used. Air inhibition can be reduced by carrying out the radiation step in an inert atmosphere, such as CO_2. Under proper conditions cures can be obtained in a few seconds.

The major deterrents to the widespread use of radiation curing are the high investment, the danger of radiation and the limitations in the usable shapes of the articles to be cured. The last problem arises because air as well as the paint to be cured absorbs the particles that initiate cure, so that available dosage is a function of distance from the plane of the window of the source. If the object to be used is not flat some parts will receive less radiation and be underexposed, and any area that is hidden from the beam will not be cured at all.[21]

In order to develop practical systems based on fluid, solvent free coatings techniques must be developed that provide the kind of viscosity control obtained in spraying solution finishes.[1] There may be several different ways of achieving such control.

Mixing two reactive materials in the gun or the spray fan is one possibility. Another possibility is to introduce a reactive component such as water, with the air supply so that it will react in the fan. This would avoid the need for a special gun.

In general, this approach leads to certain difficulties. The reaction has to be extremely fast so that some of it occurs between the gun and the work, but if it goes too far, the coating will form a gel before it has flowed and leveled to the desired extent. Control of this delicate balance may prove to be difficult. A different approach is needed, and may be provided by using two different reactions, one, which cannot lead to a crosslinked film, but which will increase viscosity, and a second reaction, which will lead to crosslinking. The first reaction could and should be very fast, so that viscosity will increase during spraying, and the freshly applied film will not sag or run. It should have sufficient viscosity to level however. The second reaction, which would be different would then crosslink the film, by the same or a different chemical reaction.

Other possible approaches should be explored to allow us to solve this problem in a variety of ways so that different types of vehicles can be used in solvent free liquid coatings. Such approaches should include such possibilities as: hot spray, which would trigger a reaction to avoid the coating becoming liquid during an oven bake; irradiation of the spray fog with UV light to initiate cure; loss of a volatile inhibitor on spraying.

Very High Solids Finishes

A possible alternative to coating systems free from all organic solvents is to use some small quantities of solvents, either in water based systems or with liquid monomers to control viscosity changes. Spray booth air flow requirements are controlled by two functions: 1.) to remove overspray, and 2.) to prevent health hazards by reducing solvent vapor concentration below the maximum allowable concentration; of these two functions the latter is by far the more demanding in terms of air volume requirements. The standard coating loses between 1 and 4 lbs. of solvent per pound of solids paint in the spray booth, and the volume of air needed to remove this solvent is so large that treatment of spray booth effluent is impractical. If however one sprays a coating containing no more than 1 lb organic solvent/4 lbs. of dry paint the maximum quantity of solvent of dry coating is reduced to 0.25 lb., or by a factor of about 10. Now, the volume of air can be reduced, and with proper engineering, may be amendable to treatment. For many applications this may be the most desirable approach, since it would provide some leeway in formulation, allow us to prepare paints by conventional techniques, and allow the customer to use his present processes with a minimum of modification. Some engineering studies have been carried out for conventional systems, and further work may be justified when and if promising candidates are developed.

Even without treatment this approach may be desirable. Some areas are contemplating an overall reduction of effluent, regardless of photochemical reactivities. The best method to accomplish this at the least expense may be to use coatings containing small quantities of solvents.

NEEDS AND LIMITATIONS OF SPECIFIC INDUSTRIES

A survey of the needs of the various marketing and sales organizations was made by contacting the industry managers, technical coordinators and the technical managers. All are aware of the need for the development of pollution free finishes and are planning strategy in that direction. One problem is the unsettled condition of the air pollution control regulations. Most states will not have such regulations on their books for another year, although a number of cities and countries are proceeding without waiting for state action.

The present trend is toward some modification of Los Angeles Rule 66. Such rules have been enacted by the cities of New York and Philadelphia, are under consideration in some other locations, and have been tentatively suggested to the states by the Environmental Protection Agency as a means of reaching the national air quality standards for photochemical oxidants.

One difficulty we may be facing is that while reformulation to conform to Rule 66 may meet proposed regulations it may not satisfy our customers. Several major paint users have already stated that their aim is to eliminate all solvent effluents. Another possible difficulty that cannot yet be gauged may arise from variations in specific details of state or local regulations that could force us to formulate different paints for different areas or carry an economic burden in a single formulation. A third problem could arise from requirements for listing compliance on labels, especially on trade sales items.

These uncertainties make the formulation of detailed research objectives a questionable activity. However, the general approach to pollution free products to replace various existing lines can be charted, based on the best estimate of the needed properties and the choices available. These were discussed with the persons responsible, and are summarized below.

Adhesives

A number of systems free of all organic solvents are already widely used and the program in this business will consist of replacing those that are solvent borne. The options are water systems such as emulsions, hot melts, preformed films and mastics. Work is being done in most of these areas.

In general, appearance is secondary to function, so that those problems that are usually associated with appearance present less difficulty. One major consideration is economics, and here water based or hot melt adhesives have an inherent advantage over solvent borne systems in the cost of the volatile portion, and possibly in insurance costs. This is already providing impetous toward aqueous systems and hot melts, and we will probably see this trend continue regardless of the enactment of pollution control regulations. 100% liquid adhesive will also become more prevalent. Hot melts will probably capture the major share of large volume adhesives business.

Appliance Coatings

Appliance coating must meet certain property-appearance demands and also have application properties that allow production line speeds to be maintained. The current emphasis is on powder coatings, with water as a less favored option. The application of water based systems at the required line speeds appears to be questionable, although recent results at the Marshall Laboratory look promising. However, water borne coatings of appliance quality have been developed, and research on application techniques would appear to be warranted.

The limited number of colors used by the appliance manufacturers makes one-color booth application of powders possible. Baking temperatures for appliance are generally high enough for powder coatings. If primers are needed, powders may be more expensive than water borne systems. The cost of added investment will also have to be considered.

One other factor may be important in planning appliance finishes strategy. Considerable thought is being given in the industry to coil coating and post-forming. This could eliminate powder coatings from consideration because of the speeds involved, but would open up other possibilities.

Automotive OE

Management of the automotive finishes division is committed to the development of powder coatings, especially to replace organic solvent borne lacquers in original equipment. This is to some extent at the customers insistance. Everybody realizes the difficulty of the task, and the major hurdles that must be overcome. These include not only the usual problems of appearance, color control, glamor and properties, but also the application of 20 or more colors on a line coupled with the need for recovery to achieve the required economics, the difficulty of repair, and the need for sanding, (at least at the present state of the art).

Water based finishes would appear to be a simpler route for the customer but previous experiences and corporate policies may have caused some prejudice against aqueous systems. Major obstacles to successful development of water based automotive finishes (assuming that the necessary property balance can be achieved) appear to be the development of stable glamour flakes, the development of practical application conditions, and possibly the recovery and recycle of overspray.

The use of solvent free liquids on automotive assembly lines would require the development of some radically different new vehicles. None of the usual "drying" materials based on oxygen or free radical initiated polymerization of unsaturated liquids can be expected to have the required durability. Epoxies and isocyanates are also deficient in this respect and toxicity considerations could limit their use in manned spray booths. The use of two component systems without solvents is possible, but could lead to problems with adequate mixing to obtain a uniform film. The big advantage could be the development of a one coat finish with attractive labor economics.

Can Coatings

The can coating industry is interested in faster production rate for existing products and also has been expanding into non-rigid containers. The needs for the latter appear to involve surface coatings in the conventional sense, as well as adhesives and barrier coatings. A major requirement for any product aside from the usual balance of properties will be the ability to be used at high production speeds.

Can coatings todayare applied mostly by roller and then baked. Many baking ovens already have incinerators. Given the difficulties of introducing new products, it is reasonable to expect most other plants will also install such equipment. If this assumption is correct then the emphasis for pollution-free coatings will be in spray applied finishes and in new plants or products.

The can industry has tried, so far with incomplete success, to utilize solvent free liquids in conjunction with radiation curing. They have also tried Elpo to cover the exposed strip near the side seam weld. They are presently not enthusiastic about either of these processes.

Our own effort on pollution free can coatings so far has been small. We have reformulated some products to conform to Rule 66, and, given the current federal guidelines, which encourage this approach, that may be adequate for the near future.

We should be aware, however, that large national manufacturers have a high degree of public visibility, and may want to go beyond the letter of the law to show their concern for the environment. If such a situation arises in the can coating field we will need finishes that do not release organic solvents on application or cure.

Powder coating would appear to have potential utility in certain areas. In some respects they would present less problems than in almost any other field. Can coatings are not pigmented, which avoids the color matching problem. The most attractive use of powder is for coating preformed drawn cans. The proximity of the spray source to the surface to be coated suggests high efficiency and therefore a greatly reduced recycle problem.

One potentially troublesome problem will, however, have to be faced. Can coatings usually are only a fraction of a mil in thickness. The current state of powder technology requires film builds in excess of one mil to get pore-free films. We will either have to develop systems that can be used at low film builds or else convince the customers that the use of higher builds is worth the increased costs on an overall basis.

The water based coatings that are currently available do not seem to be of interest. In view of the coating speeds, bake schedules and oven capacities and properties needed these coatings do not offer much hope for a commercially feasible system to replace solvent borne coatings now in the line.

Solvent free liquid coatings might be of interest for certain end uses, especially for exterior decorative purposes. No special toxicity considerations would be required, and the ususal property balance and cost would be the determining factors.

Coil Coatings

The coil coating applicators are aware of the problems that they may be facing as a result of the effluents from their operations. They have been sponsoring research to determine the types, quantities and sources of solvent effluents and also of their dispersal after emission. We can expect that they will be turning to their suppliers for products that will minimize their pollution problems.

All possible ways of eliminating solvents are potential candidates for coil coating applications. We have water borne primers, and presumably could develop water borne topcoats. Since these would not be sprayed, many of the problems encountered by other industries which are caused by spraying would be avoided. Coaters are hoping to find a marketing advantage by encouraging the use of prefinished metal.

Liquid, solvent-free systems, film lamination, powder finishes could all be used and some have been used. The limiting factors will probably be economics and line speed.

Considerable interest has been generated by the speed and low space requirements of radiation curing, and one line is in operation. It applies primers, and topcoat and can cure both simultaneously, but no inherent limitations exist that would prevent the application of topcoats. The economics of the process are under examination, and if they are favorable, a considerable swing toward further development should be expected.

At present, pigmented systems need electron beam radiation to cure, since UV light is reflected and scattered at the surface. Clear systems can be cured by exposure to UV light.

Film lamination is being used in several companies. Du Pont sells Tedlar® polyvinyl fluoride for this purpose. This is applied with a solvent borne adhesive, but non-solvent containing adhesives certainly are possible. Other laminates, that are either decorative or functional are in production. Some substances can be applied as hot melts. U. S. Steel introduced a vinyl laminated steel some years ago. One problem with such constructions is edge protection after shaping and cutting.

General Industrial

The scope of products and variety of substrates and application conditions covered by Industries 10 and 11 make any generalization difficult. Marketing is of the opinion that water borne and powder coating offer the best possibilities for introduction of solvent free coatings in the near future, with other methods further in the future. Most water borne finishes need a substantial bake to give them the desired balance of properties. So do powder coatings. For those customers that can neither bake at high temperature nor use radiation cure an air dry or low bake, solvent free system may be necessary. An alternative would be to design a total system that uses solvent vapors to coalesce a finish and removes and recovers the vapors, so that none is released.

Teflon®

Our current "Teflon" finishes are water borne coatings that nevertheless contain substantial quantities of organic solvents. These are introduced when the silicones or similar materials are blended into the formulations. Teflon S® compositions are usually solvent borne, without water. At this time, except for work to develop powder coatings based on FEP, no serious efforts are underway to develop solvent free compositions. We do have Rule 66 conforming compositions, and these may be adequate for the near future.

Industrial Maintenance

Industrial maintenance coatings will probably be included in new regulations as architectural coatings. These will be governed by Rule 66-1 as a minimum regulation. They are already restricted in Los Angeles, New York City and under the yet to be finalized Regulation 5 in Philadelphia. The implementation plans recommended by the EPA also include this section.

Presently there is no drive to eliminate solvents completely from maintenance coatings. The business differs from many of the industrial areas in that the final customers are mostly relatively small users of paints, compared to appliance or coil coatings, for example. Under some definitions they are not considered as stationary sources.

The possibility that such sources of hydrocarbons may also be prohibited, although not immediately, does exist. In that case we would have to go to either water borne or solvent free liquid finishes. Both types have been examined in the past, and this background could be valuable.

Refinish and Transportation

These two marketing areas use very similar products and have some of the same limitations as industrial maintenance. There are some important differences, however. The refinish mixing machine line places severe limitations on the changes in PVC and gallon weight that can be made to conform to Rule 66; otherwise the entire mill base structure has to be reformulated. The transportation finishes are not bound by these restrictions.

There is another major difference. Many refinish shops are small operations. In Los Angeles they have not been affected since the authorities have classified each gun, rather than the whole shop, as a separate source. There is no guarantee that other areas will allow the same tolerance. Furthermore, one source of much complaint is the odor that arises from the evaporation of the solvents into the atmosphere. Many shops are located in, or near, residential areas, so odor complaints are frequent.

Nevertheless, it is possible to project the need for non-polluting finishes for both industries. Neither can be expected to use high temperature cures, although a heat gun for small areas is possible.

The potentially most desirable solution would appear to be a room temperature curing series of solvent free products. These could probably be one or two package systems. For some customers pollution control equipment with current or Rule 66 solvents might be feasible, but for most this would be an impractical approach.

No practical solvent free air curing or two package finishes that have the desired balance of properties are presently available. It may take considerable research effort to develop these.

Perhaps the most immediate impact could be made in primers. Although these represent a small fraction of the total volume, the property requirements, especially with respect to appearance and color, are less critical than those of the topcoats. The extent to which small solvent emitters may have to go to comply may depend to a large extent on how well other measures satisfy air pollution control agencies.

Wood Finishes

Wood finishes are currently based either on NC lacquers or Dulux® type alkyds. Both will need substantial reformulation to comply with Rule 66 type legislation. For NC lacquers this may be very expensive, and acrylic systems may offer substantial cost advantages, since they appear to be easier to reformulate.

Beyond Rule 66, solvent free liquid coatings have been developed. These can be cured either by catalyzed peroxides, or by UV or electron beam radiation. They are generally based on unsaturated polyester/styrene systems. In flow coating application some small loss of styrene occurs; in spray application loss of styrene is greater. For electron radiation cure an inert atmosphere or a wax additive are needed to prevent air inhibition at the surface; wax is used for peroxide cure. When wax is used it has to be removed by sanding.

Water based coatings are generally not used on fine woods because of grain raising, but the possibility cannot be excluded, because the many finishing steps used would allow some of the total finishes systems to be water borne.

One possible approach is to offer our customers a fully integrated finishing system, which includes not only products to fit into his present process but also a line of products coupled with a process developed cooperatively. Such an approach is currently being considered.

RECOMMENDATIONS FOR FUTURE RESEARCH

Since powder coating is already the subject of a large research effort, I shall not discuss further research needs here. The manufacture of films for lamination is outside of the charter of Fabrics and Finishes. If application of a broad line of pigmented films becomes a large volume item, we could probably contribute to its development by providing adhesives and pigmented intermediates.

The areas in which relatively little work is being done are water based sprayable coatings and solvent free liquid coatings. We have had active programs in both. Water based finishes have taken over a large part of the Trade Sales market but these are not sprayed. Except for Elpo they have made only small inroads into the industrial markets.

Our efforts to develop solvent free liquid finishes have not been successful in the past, and right now no work is being carried out in this general area. The following discussion concentrates on broad, general objectives only. Specific products and industries will need to set product objectives that may be more limited in scope.

Studying of Application Properties

The major problem with both water based and solvent free liquid coatings has been application properties. Liquid coatings when sprayed must increase in viscosity between the gun and the work so as to stay in place on the work. The rate of evaporation of water is more dependent on temperature and relative humidity than that of organic solvents, and is fixed at any given condition. This presents problems as the weather changes.

S. Hochberg[24] has suggested that air conditioning costs for spray booth control can be minimized by working at high temperatures so that the absolute humidity can be kept reasonably high. This would create conditions that would require heating and humidification most of the time. These processes are cheaper than cooling and dehumidification.

Furthermore, our experience with spraying water based systems has shown that popping is a serious problem which must be solved before we can commercialize such coatings.

One set of objectives for future research therefore should be 1.) to determine the factors that need to be controlled to spray aqueous finishes of commercial potential and how these factors offset the quality of the applied finish, 2) the physical properties of the finish that need to be controlled and how these affect the application properties; b) what additives, if any, can be used as formulating aids to reduce or avoid specific problems. If the experiences with rolling and brushing of trade sales paints can be used as a guide we should be able to determine certain principles that have general validity; other aspects can be expected to vary for different systems.

The problems associated with the application of solvent free liquid vehicles are probably more difficult to solve than those of solvent or water borne systems. If the liquid is sufficiently fluid to be sprayed, it generally will also flow on the work (or off the work). In the past this problem has been solved by the introduction of thixotropy, usually at a sacrifice in some other property, such as gloss. One objective for research in this area will have to be the discovery of new and practical methods of increasing the viscosity between the gun and the work or at least right after application. The desired increase in viscosity should be limited, so that flow out and leveling can take place.

Film Properties

High bake, water borne finishes can probably be designed and formulated to give good film properties for almost all industrial uses. The major difficulties we have encountered in the past and can expect to encounter in the future have to do with pigmentation. Many inorganic pigments have some solubility in water or contain water soluble impurities, which can affect stability and performance. There are some organic pigments which are known to be difficult to disperse in water without use of organic solvents. Aluminum flakes react with water and only a few grades are sufficiently stable to be useful in aqueous systems. If we decide to develop a broad line of water based coatings we will have to know what effects the soluble fractions of various pigments will have on the stability and balance of properties of specific vehicles. While this does not call for any active research objectives immediately, it may be timely to collect the maximum information about kind and quantity of solubles from pigments suppliers. We will also need dispersants to obtain a broad range of colors. The range available from trade sales lines will not be adequate for industrial markets. Some leads toward such dispersants may come out of the work on AB dispersant technology.

Non-baking water based coatings present a different problem. The most generally used types are the latices used in Trade Sales. These by necessity are highly pigmented formulations which have to be soft enough to be capable of coalescing at or near room temperature. Such systems would not be suitable for many industrial end uses. Some emulsions of drying oils are available, but these have not been widely accepted. The use of water soluble polymers is hindered by the fact that they generally retain their solubilizing functions on drying, and therefore remain water soluble or water sensitive. One research objective therefore should be the synthesis of a practical water soluble vehicle that will lose its solubilizing groups without heating after application, so as to become water insensitive. Finishes based on this principle would find utility in many applications that today use air drying alkyds or lacquers, especially those sold by General Industrial or Refinish.

Solvent free, liquid vehicles are currently being used for UV or electron beam radiation curing. Generally these are unsaturated, low molecular weight polymers that are dissolved in high boiling monomers. They lose a small quantity of the monomer during roller coating or coil coating application, but most would not be suitable for spraying. They can also be cured by peroxide initiated low temperature redox polymerization, and vehicles of this type (maleic polyester/styrene) are used in furniture finishes. These tend to be inhibited by air so that the surface is usually undercured and has to be removed. Other methods of overcoming air inhibition are the addition of an incompatible, film forming wax that also has to be removed, or carrying out the curing process in an inert atmosphere.

Our research efforts should be directed toward scouting and development of new, low temperature curing systems which will have film and resistance properties and at least equal to air drying alkyds. It may be possible to use existing alkyds with reactive, non volatile diluents if we can solve the application problems.

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