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Environmentally Friendly Coatings: Past, Present Developments, and Future

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The last 20 years we witness enormous research activities with an aim to reduce the solvent emission from organic coatings. It is practically impossible to summarize the whole work done in a paper like this, despite its ambitious title. Therefore, the overview of the achievements in water-borne, powder, and high-solids coatings will be limited to the last five years only. Radiation-curing coatings, which belong to the environmentally friendly products, represent an important area as such. Because of the relatively small volume and rather minor environmental impact, they will not be regarded. The paper is concluded with the thankless task of predicting the future trends. As usually, it should be regarded as a combination of wishful thinking and extrapolation of the present knowledge and ideas to the years to come.

1. Water-Borne, Powder, and High-Solids Paints: the Motives

The development of water-borne, powder, and high-solids coatings is very often related to the environmental pressure of the second half of the 20th century. Such a statement can certainly help in cleaning up the stings of remorse at most of us for polluting the environment. The honest journey in the recent history shows, however, that the environmental issue at least has not initiated the appearance of water-borne, powder, and radiation-curing coatings, and that these developments were not inspired by our concern about the future of the mankind.

Acrylic latex water-borne coatings of nowadays were introduced on commercial scale in the 1950s. No environmental concern was standing behind it. It was just a new technology which brought products of better performance compared to the casein-based paints developed by the old Egyptians, and cheaper compared to the paints of the Australian Aborigines and the American Indians based on natural rubber latex as a binder¹⁾. In fact, the very first environmentally friendly coatings were developed by the prehistoric man who has had plenty of nature, the whole nature and only the nature. He was certainly not concerned about the environmental pollution when he developed the first water-borne paints based on eggs, milk, or sap from shrubs and trees as binders²⁾. These early friendly products were unfortunately ignored by the civilisations to come. They have switched towards paint systems that will be later on recognised as environmentally unfriendly.

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The first step in this development was the appearance of the oil-based paint being in the beginning very innocent solvent-free material. However, this was the forerunner of the future devil. The people of the 20th century missed the patience of Rembrandt, the master of the oil paints, who was rather happy with their drying time. We wanted to have it quicker, better, and cheaper. And the environment was anyhow gratis.

It took 300 years from the death of Rembrandt when in 1966 the successors of the American Indians now living in the skyscraper wigwams of Los Angeles have discovered that one of the reasons for not being able to see the sun even in an uncloudy day was the paints of nowadays. Then they have invented the famous Rule 66, which was a step forward in the process of discovering that water was not a toxic agent. That was the initial step of the reincarnation process of water as a solvent. At the very beginning more as a fashion slogan, but later on as a real necessity. Now we even dare to say that water can be the only solvent³⁾.

The history of powder coatings is much shorter. First developments began in the early 1950s when powdered polyethylene was successfully applied in a fluidized bed process on a preheated metal surface⁴⁾. However, trying to find environmental aspects in this development will be a waste of time. The reason why polyethylene was applied in powdered form on the metal was very simple. It does not dissolve in any common solvents. The success of the thermosetting powder coatings which appeared later mostly resulting from the work done in Shell Chemicals, Scado BV (later DSM Resins BV), and UCB⁵⁾ has to be traced in the superior price/performance ratio of these materials, rather than in the environmental aspects of the system.

High-solids coatings are in fact the only new systems whose development was pushed by environmental reasons. They are children of the green trend of this century in the real sense of the word. From environmental point of view, however, they score the least, unless in their ultimate development they reach a solids content of 100%, thus becoming liquid competitors to their powder brothers.

2. Water-Borne Coatings

The terminology used for water-borne coatings is often confusing. The term water-borne coatings which is very much in use nowadays refers to liquid coatings in which a substantial fraction (not necessarily all) of the volatile medium is water. Water-borne coatings themselves are mostly classified in the following three main groups:

Aqueous dispersion coatings

The binder is a dispersion of solid polymer particles in an essentially aqueous medium. Particle size is usually in a range of 50–500 nm. In the most cases the binder is produced by emulsion polymerisation, when people usually talk about polymer latexes. Polycondensation however, can be also used for production of aqueous dispersions such as polyurethane dispersions.

Aqueous emulsion coatings

Represent relatively small group of water-borne coatings, in which the binder is an emulsion of a liquid polymer in water. Alkyd and epoxy emulsions are the typical

representatives of this group.

Water-reducible coatings

Represent relatively large group of products based on different binders in form of colloidal dispersion in water. In most cases water-reducible binders are transparent because of the small particle size of the binder. They are made by solution of hydrophobic polymers having hydrophilic segments in water-miscible organic solvents followed by addition of water. As a consequence, the hydrophobic polymer separates and forms colloid particles which are stabilized by its hydrophilic parts.

Most of the developments in water-reducible coatings have been done in the 1960s and 1970s. These coatings have reached already their maturity. They do not offer, however, a system which is absolutely solvent free. In addition, they contain amines and neutralizing agents. It is very difficult to expect that the concept of water-reducible coatings will ever result in paint systems which can compete with the aqueous dispersions and emulsion paints. Therefore water-reducible coatings will not be considered in this paper.

2.1. Achievements in aqueous dispersions

Water-borne paints based on polymer dispersions as binders are certainly the most important paint systems for architectural application. Water and water vapour permeability resulting from the porosity of the film, and inferior dirt pick-up and blocking resistance because of the thermoplastic character of the binders are typical problems encountered with aqueous dispersion paints. They have been enough of a challenge to provoke new developments in this area. Three different approaches can be easily distinguished in tackling these problems.

2.1.1. Core-shell polymer dispersions

The blocking resistance of aqueous dispersion paints can be improved by changing the particle morphology. Different types of core/shell polymers have been developed for this purpose. Trapani and Jansson⁶⁾ have reported results obtained by core/shell technology and alkali-swellable latexes which allow application of these materials even in the wooden furniture industry where the blocking resistance connected with the packing and transportation of the coated material is a stringent prerequisite. The core-shell polymer particles consist of alkali-insoluble core and alkali-soluble shell, in which the shell is chemically grafted to the core. The core itself contains polyfunctional monomers having groups with unequal reactivities, such as allyl, vinyl, or crotyl esters of (meth)acrylic or maleic acid, 1,3-butadiene, and isoprene. The core-shell dispersion is prepared by emulsion polymerisation of the core followed by emulsion polymerisation of the shell and grafting the shell to the core^{7, 8)}.

A core/shell polymer has been used in a can-coating lacquer where the core having a T_g greater than 40°C is internally cross-linked by means of corrective alkylol acrylamide. The shell portion has a low T_g (<20°C). The cured coating has excellent flexibility due to the shell portion and desirable hardness imparted by the core portion⁹⁾. A similar hard core/soft shell approach in which the core is made out of polyfunctional monomers such as allyl methacrylate has been disclosed in a patent of Rohm GmbH^{10, 11)}.

A base coat composition comprising an aqueous dispersion of microparticles of two sorts: (i) a non-cross-linked seed portion surrounded by cross-linked shell and a stabilising mantle-containing salt-forming carboxyl groups and (ii) a non-cross-linked seed portion surrounded by cross-linked shell and a stabilising mantle-containing polyoxyalkylene stabiliser units derived from methoxypolyethyleneglycol methacrylate has been described in a patent of ICI¹²⁾. It has been claimed that this coating is suitable to be used in a base coat/clear coat system for car repair.

The lack of film build in the aqueous dispersion paints has been attacked by polymer dispersions with multilobal particles¹³⁾. The multilobal particles have effective hydrodynamic volume equivalent to a particle with diameter of 1000 nm, containing lobes of ca. 350 nm. As a result, the film build reflects that of 1000 nm particles, while the pigment binding ability is that of a 350 nm particle. The film build is controlled by the ratio of multilobal to non-multilobal particles in the binder. Multilobal acrylic polymer latexes have been commercially introduced in 1987.

2.1.2. Acrylic hybrid dispersions

The analysis of the patent literature shows that considerable work has been done in combining the properties of polymers obtained by emulsion polymerisation with those obtained by polycondensation in one system. Hybrids consisting of alkyds, polyesters, epoxies, and polyurethane resins next to the acrylic/styrene and other polymer dispersions can be found in the literature.

A patent of Vianova Kunstharz AG¹⁴⁾ describes an oxidatively drying water-borne coating based on a binder which is a combination of an acrylic polymer and alkyd resin. The binder is prepared by emulsion polymerisation of preemulsion of blend of acrylic monomers in which the alkyd resin has been dissolved. Instead of an alkyd/acrylic hybrids, epoxy and polyurethane acrylic hybrids can be prepared in the same manner.

A solution of the problem of inferior adhesion of acrylic alkyd hybrids for industrial application has been suggested by the use of oxirane-de-functionalized epoxy resin phosphate esters which are not self dispersible in water¹⁵⁾. In a patent of BASF a polyester-acrylic hybrid coating has been described where both acrylic and polyester coating contain the same hydroxyl functional groups with hexamethoxymethylolmelamine as a cross-linker¹⁶⁾.

Metallic, water-borne automotive paint base coat has been formulated with the binder being a hybrid consisted of alkyd or polyester water reducible resins in a combination with an acrylic latex¹⁷⁾.

Aqueous polymer dispersion of a hybrid type has been disclosed in a patent of Holden Europe SA¹⁸⁾ comprising 80-95% acrylic polymer and 2-20% epoxy resin. The coating is recommended for the use in food drink containers or in production of metal sheets for can manufacture.

Intimate combinations of urethane and acrylate are obtained by means of emulsion polymerisation of acrylic monomers in a urethane environment. This urethane-acrylic single system provides great advantages in terms of (i) less water sensitivity because the emulsifier is not needed; (ii) improved stability because the ionic urethane is powerful stabilizing

agent; and (iii) chemical resistance because the morphology of the particle is such that the urethane properties dominate¹⁹⁾. Different patents of ICI protect the preparation of such hybrids^{20, 21)}.

Polyurethane acrylic hybrid emulsions for the preparation of industrial stoving enamels are reported in the patent of AKZO²²⁾. The binder is prepared by the emulsion copolymerization of acrylic functional polyurethane intermediate with 2-hydroxyethyl methacrylate.

2.1.3. Cross-linkable acrylic dispersions

Considerable works have been done to avoid the problems generated by the thermoplastic character of acrylic dispersions by introducing cross-linking during or after the film formation.

For example a room-temperature-drying coating by autooxidation has been prepared from aqueous latexes based on vinyl copolymers with partially gelled particles. The latex is autooxidisably cross-linkable due to the monomer system containing a lower reactivity multifunctional monomers (allyl methacrylate and diallyl phthalate) added at the late stage of the polymerisation process²³⁾.

Polyfunctional carbodiimides have been proposed as cross-linkers for carboxyl functional acrylic dispersions to formulate storage stable one-pack coatings curable at ambient temperature. The paint has to be formulated with pH higher than 7 by means of volatile amines. Upon evaporation of the amines, the pH drops to low enough to promote the reaction between the carbodiimide and the carboxyl groups⁶⁾.

Several patents of BASF²⁴⁻²⁷⁾ describe water-borne wood coatings, antiefflorescence cement coatings, and automotive base coatings consisting of two components; a polymer dispersion being a copolymer of (meth)acrylic esters, (meth)acrylic acids, (meth)acrylic amides such as acrylamide, copolymerizable aldehyde or ketone such as diacetone acrylamide, and polyfunctional acrylic monomers such as butanediol diacrylate as one component and 0.5-1 mole of adipic acid dihydrazide per mole diacetone acrylamide as a second component. The coatings can be cured at room or elevated temperature and are characterised with resistance to wear, stacking, and chemical attack.

Storage stable aqueous dispersions being acrylic copolymers containing acid groups are suitable to be combined with polyhydrazides in order to obtain cross-linkable coatings. The system is stable during storage at pH higher than 7 and undergoes cross-linking at room temperature upon drying producing films which are resistant to blocking and completely insoluble in organic solvents²⁸⁾.

Novel acid-curing polymer dispersions for wood coatings using fully etherified alkoxy methyl amide groups in an acrylic backbone have been developed²⁹⁾. The system is nearly free of formaldehyde emittance during curing; there is no free formaldehyde in the wet paint; there are no suspected cross-linkers present; and there is virtually no solvent (2-4% coalescing agent on paint formulation).

Acid-curing water-borne coating composition with very low formaldehyde emission has been described in a patent of DSM Resins BV³⁰⁾. The coating is a blend of hydroxyl functional acrylic dispersion and alkoxyate polyurea derivatives.

Acid-curing aqueous two-component coating based on self-cross-linkable acrylic dispersion containing etherified methylolacrylamide groups and water-soluble melamine resin as the second component has been disclosed in a patent of BASF with a main use in furniture lacquers³¹⁾.

Cross-linkable acrylic dispersion containing epoxy groups originating from α or β unsaturated epoxy compound such as (meth)allyl glycidyl ether, 1,2-epoxybutyl acrylate or glycidyl crotonate has been disclosed as binders for two-component water-borne coatings using polyamines or polyhydrazides as hardeners³²⁾.

Self-cross-linkable polymer dispersions are described in a patent of ICI³³⁾. The polymers have pendent amino groups attached to the backbone capable to undergo cross-linking with acetoacetates or acetoacetamides. The cross-linking takes place at ambient or elevated temperature.

Self-curing water-borne paints have been prepared from polymer dispersions containing alkoxy silane groups. The self-condensation cross-linking is carried out at low pH (pref. pH=2), followed by neutralisation by addition of a base to give pH=6-8³⁴⁾.

Storage-stable and cross-linkable compositions curable at elevated temperatures being hydroxy functional acrylic aqueous dispersions cross-linked with tetramethoxymethyl glycoluril are disclosed in different patents of Glidden Co³⁵⁻³⁷⁾. Both components, the binder and the cross-linker, are previously treated with protonised cation exchange resin to reduce the pH to below 1.8, and by addition of small portion of cation salt such as CaHPO_4 , the pH of the mixture is increased to 2-5. After curing the coating, which is essentially free of acid, the curing catalyst gives a tough cross-linked film which has a high enough pH to avoid problems of corroding the steel.

2.1.4. Polyurethanes

New developments in polyurethane dispersions have been reported by Jansse¹⁹⁾. By incorporation of multifunctional isocyanates, pre-cross-linked and water-dispersed polyurethanes are obtained, which offer new or improved properties with respect to solvent resistance and metal protection.

Difunctional blocked polyurethane dispersions with isocyanate functionality, or polyurethane dispersions with pendant blocked isocyanate groups have been also evaluated in stoving coatings with an intention to replace conventional solvent-borne stoving systems¹⁹⁾.

A self-cross-linkable water-borne coating comprising an aqueous polyurethane dispersion having hydrazone functional groups and carbonyl functional groups has been described in a patent of ICI Resins³⁸⁾. The coating composition has good storage stability and undergoes self-cross-linking at room temperature during and/or after film formation.

New improved polyurethane dispersions based on *m*-tetramethylxylene diisocyanate (TMXDI) with higher tensile strength and high elongation, high solids, and low content of volatile organic compounds have been reported by American Cyanamid Co. The same laboratory reports the work done on copolymerization of TMI unsaturated isocyanate with acrylic monomers. The obtained latexes show improved chemical resistance due to cross-linking through the pendant isocyanate groups³⁹⁾.

An interesting technique to produce water-borne two-component polyurethane coatings

has been reported by Jacobs and Ju⁴⁰⁾. The technique is based on the findings that polyisocyanates react only slowly in aqueous two-component formulations. Two-component coatings are produced by mixing water dispersible polyisocyanate with dispersion of hydroxy functional polymer.

2.2. Aqueous emulsion paints

2.2.1. Epoxy emulsions

Raghavan and Lewis⁴¹⁾ report the results on water-borne epoxy primer capable of curing at room temperature containing no volatile organic compounds. This zero-VOCs two-component paint based on an aqueous dispersion of low molecular weight epoxy resin having a pot life of 10 days, provides excellent corrosion and chemical resistance, and can be applied by conventional application techniques, such as air-, airless- or electrostatic-spray, dip, or flow coating.

The use of water-borne ambient temperature curing systems has been discussed in a paper of Schneider⁴²⁾. The present systems include water emulsions of liquid low molecular weight bisphenol A epoxy resins which can be cured with polyamidoamines. In order to avoid emulsification problems because of high viscosity of the system, reactive diluents might be employed on expense of the industrial hygiene, longer curing time and reduced chemical resistance. Another negative aspect of the system is that the hardener has to be mixed with the resin prior to emulsification at the application site. Emulsions of high molecular weight epoxy resins show superior paint performance. However, the film formation at room temperature is achieved by addition of organic cosolvents, which is certainly a disadvantage from ecological point of view.

2.2.2. Revival of the alkyd paints?

Water-borne coatings for architectural applications, such as vinyl, styrene-acrylics, and pure acrylic latexes are certainly the dominant systems for wall paints for inside and outside application. However, when used on wooden and metal substrates they suffer from several drawbacks compared to conventional alkyd paints as presented in **Table 1**.

It can be seen that alkyds score worse than acrylics with respect to yellowing resistance, weatherability of the film, UV resistance, and absence of solvent.

The yellowing tendency of the alkyds is inborn deficiency and can not be avoided to full extent. However, the experience of using alkyds for more than 60 years has shown that with a good choice of raw materials the yellowing tendency of the alkyds can be brought to an acceptable level.

The UV resistance and the weatherability can be substantially improved by the use of UV absorbers and special types of diacids in the formulation of the binder.

The problem which remains is the presence of the solvent in conventional alkyds. The attempts in 1970s with water reducible alkyds containing amines as neutralizing agents and cosolvents did not end up with a commercial success. Improved versions of these systems with grafted methacrylic acid onto the alkyd resin can be traced in the contemporary patent literature⁴⁴⁾. Ecologically speaking, these systems were no substantial improvement compared to conventional alkyds. Moreover, they suffered from several

Table 1. Comparison between acrylic dispersion paints and conventional alkyd paints

Property of the system	Acrylic (dispersion)	Alkyd (conventional)
Gloss	—	++
Flow properties	+	++
Yellowing resistance	++	—
Adhesion	+	++
UV resistance	++	—
Water permeability	+	++
Water vapour permeability	—	++
Film-forming temperature	—	++
Blocking resistance	—	++
Dirt pick-up	—	++
Film porosity	—	++
Corrosion protection	+	++
Penetration in the surface	—	++
Solvent resistance	—	++
Applicability	+	++
Removability of old paint	—	++
Absence of solvent	+	--

short comings such as hydrolytic instability, viscosity anomaly, prolonged drying time, and strong yellowing tendency.

Much more attractive option when water-borne alkyd resins are considered as binders for environmentally acceptable paints is full avoidance of cosolvents and amines. Until recently, however, it was not possible to produce alkyd emulsions which do not contain cosolvents and amines exhibiting good overall properties. Recent publications give an indication that these problems have been successfully solved. Suitable emulsions can be made from most alkyds with lower viscosity, in which sufficient shear forces can be applied in order to achieve desired particle size ensuring storage stability^{3, 45, 46}. Commercial types of amine- and cosolvent-free alkyd emulsions have been introduced in Europe⁴⁷.

An interesting method to eliminate the use of conventional surfactant in preparation of alkyd emulsions by in situ polymerisation of hydrophilic monomers within solventless alkyd resin followed by inverse phase emulsification has been reported⁴⁸.

Short-oil alkyd resin emulsion has been used in preparation of acid-curing wood lacquers in combination with water-soluble amino resins⁴⁹.

Urethane groups containing alkyd emulsions prepared by the reaction of low molecular weight alkyd resins with dimethylol propionic acid as a source of carboxyl groups and IPDI, having molecular weights between 10,000 and 70,000 have been described in a patent of Bayer⁵⁰. Coatings obtained with these binders are characterized with good water and solvent resistance, high hardness, elasticity, and gloss.

The use of polymerizable surfactant in preparation of alkyd emulsions has been discussed by Holmberg⁵¹. It is claimed that properties of dried film have been considerably improved by reducing the surfactant migration from the bulk to the film surface.

2.3. Miscellaneous

Water-borne styrene-free unsaturated polyester coatings which undergo curing upon UV irradiation have been described by Dvorshak and Riberi⁴³⁾. The binders used are trimethylolpropane diallyl ether terminated unsaturated polyester resin emulsions which are stabilised by means of nonionic emulsifiers incorporated into the polymer backbone.

First water-based polytetrafluoroethylene paint has been recently introduced in the market in Europe^{52, 53)}. It is claimed that the coating provides a long-lasting barrier against chemicals, corrosion, abrasion, and extremes of temperature and humidity and can be applied virtually on every surface including concrete, brick, timber, metal, and plaster-board. The main features of this coating are outstanding durability and ease-of-cleaning.

Water-borne polymer dispersions based on fluoroethylene and vinyl ether copolymers have been introduced by Asahi Glass Company. These polymer dispersions are characterized with exceptionally superior water and weathering resistance compared to conventional acrylic counterparts. They claim that the water absorption dropped from 21% to ca. 1%, and the gloss retention in clear coat formulation and pigmented formulation improved from 500 h to longer than 2000 h and from 1000 h to longer than 2000 h, respectively⁵⁴⁾.

Further improvements in the technology of making nitrocellulose lacquer emulsions have been reported by Winchester⁵⁵⁾. An inversion emulsification process has been used in order to produce lacquer emulsions from 65–70% solids nitrocellulose lacquers. All performance advantages of the conventional nitrocellulose solution lacquers are preserved, since the process employs virtually the same raw materials. The formulation of low-VOC water-borne coatings for wood based on nitrocellulose-acrylic latex has been discussed by Haag⁵⁶⁾.

It has been reported that water-borne silicone-modified polyurethane/epoxy coatings provide the same degree of anticorrosive protection in sea water immersion tests as conventional solvent-borne systems⁵⁷⁾.

3. High-Solids Coatings

The term “high solids” refers to paints with reduced amount of solvents rather than to a well-defined coating system with respect to the solids content. Generally it is accepted that this definition should refer to coating systems with more than 80% nonvolatiles by volume. In its upper limit, high-solids coatings approach 100% solids content, when one talks about solvent-free coatings (such as powder coatings) or coatings which contain reactive diluents (in most cases radiation-curing coatings).

Although it is difficult to classify high-solids coatings properly, it is instructive to distinguish among air-drying, two-component room-temperature-curing, and stoving high-solids coatings. For the purpose of presentation, air-drying high-solids coatings will be separately treated from the other two groups.

Next to the common approach for obtaining high-solids coatings by reducing the viscosity of the binder solution, a new way of application of solvent-based coatings has been developed by Union Carbide, leading to a system with a reduced organic solvent

emission⁵⁸⁻⁶⁰). This spray finishing technology uses supercritical carbon dioxide to replace part of the organic solvents in industrial coatings. Supercritical carbon dioxide is CO₂ gas heated above its critical temperature (31°C) and compressed (73 atm), so that its density approaches that of a liquid. This liquid possesses solventlike properties and can be used to replace up to two thirds of the volatile solvents in the paint formulation. The reduction of volatile organic compounds in this way accounts for up to 70%. Supercritical carbon dioxide has high solubility in most coating formulations and acts as efficient viscosity reducer. Therefore, reformulated coating has high solids content even when polymers of higher molecular weight are used, thus contributing to superior coating performance.

3.1. Air-drying high-solids coatings

In the case of architectural applications and light maintenance work, alkyd paints are still the leading option available on the high-solids market.

Low VOC architectural high gloss paints with a solids content between 85–95% at application viscosity have been described and the synthetic route for obtaining these oligomers has been discussed by Hofland and Reker⁶¹). No special binders are needed for pigment grinding, resulting in a very simple paint formulation. The binders used contain unsaturated groups originating from fatty acids as well as acrylic and allylic double bonds.

A Diels-Alder adduct of acrylic acid and conjugated linoleic acid has been used as direct replacement of phthalic acid anhydride in preparation of alkyd resins. Resins with lower viscosities and higher molecular weights can be produced, resulting in films with improved properties such as drying time, hardness, and impact resistance⁶²).

A high-gloss paint with 85% solids content at application viscosity has been described in a patent of BASF⁶³). The binder of the paint is prepared by polymerisation of ethylhexyl acrylate in a reaction medium being long-oil alkyd resin containing dipentaerythritol as a polyol.

Fast-drying high-solids paints can be produced according to the disclosure of Vianova Kunsthartz⁶⁴) by using an alkyd resin in combination with a fatty acid graft copolymer based on unsaturated fatty acids, tetrahydrophthalic anhydride, methacrylic acid and vinyl and/or (meth)acrylic monomers. It is claimed that fast-drying high-solids paints can be made with no tendency to wrinkle at film thickness up to 400 μm .

Solvent-free coatings can be prepared by using resin composition being a Diels-Alder adduct of maleic anhydride to linseed oil esterified with hydroxyethyl methacrylate. It is claimed that the resin can be used as a sole binder in solvent-less decorative paints as well as grinding a wetting agent for pigments for solvent or water-borne coatings⁶⁵).

Binder for solvent-free coatings is prepared by esterification of tall oil fatty acids, dipentaerythritol, and isophthalic acid. To decrease molecular weight and viscosity, monoalcohols has been used in the preparation of the resin. An ester obtained by esterification of soyabean fatty acids and trimethylol propane diallyl ether serves as a reactive diluent in combination with the low molecular weight alkyd⁶⁶⁻⁶⁹). Another reactive diluents for air-drying paints or oil-free polyesters for industrial stoving enamels are prepared by

reacting unsaturated or saturated fatty acids with propoxylated polyols⁷⁰⁾, or propoxylated polyols in combination with isocyanatoethyl methacrylate⁷¹⁾.

3.2 Two-component and stoving high-solids coatings

New family of aliphatic epoxy resins which does not absorb ultraviolet light to the same extent as aromatic epoxy resins had been developed⁷²⁾. High-solids coatings based on this binders curable at ambient temperatures possess excellent gloss retention, chalking, and yellowing resistance. These materials are obtained by the reaction of polyalcohols, such as 2,2,2,6-tetramethylolcyclohexanol, with epichlorohydrin, followed by the dehydrohalogenation of the corresponding tetrahalohydrin ether. Polyamines and polyamidoamines are suggested as curing agents. The same epoxy compounds, however, can be used in combination with carboxyl functional acrylic resins for formulation of high-solids automotive clear top coatings.

Solventless coatings which cure in the presence of oxygen have been obtained by using acrylic oligomers, reactive diluents such as poly(acrylic ester)s and poly(allylglycidyl ether)s. In this way the problem of air inhibition is overcome allowing fast curing at elevated temperatures (20 min at 80°C) through chain initiation propagation mechanism. The system makes use of a conventional initiating system comprised of peroxides or hydroperoxides in combination of cobalt salts as accelerators⁷³⁾.

A new class of organic peroxides based on t-amyl hydroperoxide has been developed. These peroxides during decomposition yield hydroxy or carboxyl free radical fragments. By means of them it is possible to produce low molecular weight high-solids acrylic resins with a hydroxy or carboxyl group attached to the polymer chain end⁷⁴⁾. Callais et al. discuss the advantage of using t-amyl peroxides over conventional organic peroxides and azonitrile initiators⁷⁵⁾.

2-Methyl-1,3-propanediol has been introduced as a new monomer for preparation of high-solids polyesters. Several advantages offered by this new raw material are being a liquid form, asymmetry of the monomer, reduced crystallinity of the polyesters obtained, and shorter cooking times. With respect to the paint performance, improved flexibility has been obtained compared to the NPG-based coating⁷⁶⁾.

A high-solids polyester-based coating for stoving enamels for industrial application has been made by stepwise ring-opening addition reaction of diacid anhydrides and monofunctional epoxy compounds to a precursor being polyfunctional polyol or polyester oligomer with OH functionality⁷⁷⁾.

4. Powder Coatings

Powder coatings are the stars in the paint world with very attractive growth between 10-20% per year, depending on the geographical area. The literature and patent search in the last 5 years shows intensive research activities in the field. Spectacular achievements, however, are not yet booked. It must be concluded that the real breakthrough has still to come.

4.1 Binders

Polyesters and epoxy resins are still the main binders for powder coatings. Because of their excellent price/performance ratio, it is hard to believe that these resins will be replaced by completely different systems. Unless a breakthrough happens in other than existing application areas, these two binders will remain working horses in the powder world.

Relatively little changes can be observed in epoxy resins for powder coatings. Powder coatings with superior heat resistance and toughness are disclosed in a patent of Dainippon Ink⁷⁸⁾ using epoxy resin made by reaction of tetrakis (4-hydroxyphenyl) methane with epichlorohydrin followed by subsequent dehydrohalogenation with sodium hydroxide.

Improved low temperature cure response has been achieved in powder coatings formulated out of epoxy resins containing SO₂ groups derived from 4, 4'-dihydroxyphenyl sulfone, and carboxyl functional polyesters^{79, 80)}.

New raw materials such as 1, 4- and 1, 3-cyclohexanedicarboxylic acid, 1, 4-cyclohexyldimethanol, hydrogenated bisphenol A, and 2-butyl-2-ethyl-1, 3-propanediol as raw materials for formulation of powder coating polyesters with improved outdoor durability are available. An extensive report on influence of these polyester building blocks on the glass transition temperature of the end product has been submitted⁸¹⁾.

Polyester resins containing cycloaliphatic dicarboxylic acids with improved outdoor durability have been developed by DSM Resins BV⁸²⁾.

Superior outdoor durability of polyester powder coatings has been achieved by incorporation in the polyester resins of fluorine-containing diols with general formulas HOCH₂-(CF₂)_n-CH₂OH, HOCH₂-CF₂O-(C₂F₄)_m-(CF₂O)_n-CF₂-CH₂OH and HOCH₂-(CF₂O)_m-CH₂-OH. Superior outdoor durability combined with excellent stain resistance have been claimed⁸³⁾.

Polyesters with improved storage stability due to high T_g (up to 70°C) have been described in a patent of Eastman Kodak Co⁸⁴⁾. The T_g of the polyester resins has been increased by incorporating a diol such as 2, 2-dimethyl-1, 3-cyclohexyldimethanol or 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol.

Hydroxyl functional polyester resins containing built-in catalysts are used for powder coatings cured with tetramethoxymethyl glycoluril^{85, 86)}. Polyesters are prepared by direct esterification of polyols with polyacids, among one of them being sodium salt of 5-sulfoisophthalic acid. Improved storage stability combined with proper melt flow characteristics under curing conditions are claimed.

The problem of inferior flow of powder coatings has been tackled by using blends of amorphous and crystalline polyesters cured with polyisocyanate^{87, 88)}. In a combination of semicrystalline polyesters and oxime-blocked polyisocyanates as hardeners, an improved flow at low curing temperature is obtained⁸⁹⁾.

Polyester reins are not the most suitable materials for application with tribo guns. However, in a patent of DSM Resins⁹⁰⁾ a good chargeability has been achieved by means of sterically hindered amines or amino alcohols. At the same time the storage stability

of the system has not been adversely affected. In a patent of Nippon Oils & Fats⁹¹⁾ tribochargeable polyester resins are disclosed, where chargeability has been imparted by nitrogen-containing compounds such as isocyanates, guanamine, benztriazole, etc.

Poly(vinylidene fluoride) was so far the only fluorine-containing polymer in use for thermoplastic powder coatings with extraordinary outdoor durability. Novel fluorine-containing resins for thermosetting powder coatings are since recently available⁵⁴⁾. These binders are copolymers of fluoroethylene and vinyl ethers (specifically 2-hydroxyethyl vinyl ether as source of hydroxyl functionality). Powder coatings developed on the basis of FEVE polymers (fluoroethylene vinyl ethers) are cured with isocyanate functional cross-linkers. Compared to acrylic powder coating for exterior use, which undergoes 50% gloss reduction in accelerated weathering tests, fluorine-containing polymer based powder coating does not show any gloss decrease after 3000 hours. Next to the isocyanate curable powder coatings⁹²⁾, powder coatings containing epoxy groups suitable for cross-linking with polyacids are based on copolymers of trifluoroethylene or pentafluoropropylene and glycidyl methacrylate⁹³⁾.

The family of thermoplastic powder coatings has been extended by a new type of thermoplastic polyurethane coatings produced by in situ reaction of pigmented NCO-terminated polyester with 1,4-butanediol⁹⁴⁾ or cyclic secondary diamines⁹⁵⁾ as chain extenders in inert organic solvent. The formed polyurethane elastomer being not soluble in the organic solvent is easily filtered, washed, and dried to produce thermoplastic powder coating with an elongation at break of 625% after fusion at 190°C for 30 minutes.

4.2. Cross-linkers

Glycidyl urethanes as reaction products of polyisocyanates and hydroxy glycidyl esters are disclosed in a patent of DSM Resins⁹⁶⁾. Glycidyl esters of hydroxypivalic, hydroxypropionic, hydroxybutyric, and hydroxymethylbenzoic acids are named as suitable materials which after reacting with aliphatic diisocyanates produce solid diglycidyl urethanes.

An alicyclic compound being a condensation product of trimethylol propane and 4-vinylcyclohexane-1-oxide has been claimed as suitable cross-linking agents for carboxyl functional polyesters⁹⁷⁾.

A new type of cross-linking agents for carboxyl functional polymers in powder coatings have been described in two patents of Nippon Paint^{98, 99)}. These cross-linkers are oligomers or polymers with molecular weight between 300 and 10000 and at least 1 spiroortho ester group.

In a patent of Ciba-Geigy¹⁰⁰⁾ a trifunctional glycidyl ester of tricarboxylic acids has been described as cross-linker for powder coatings. The material has been prepared by ring-opening addition of dicarboxylic acid anhydrides to dimethylol propionic acid followed by reaction of the obtained tricarboxylic acid with epichlorohydrin and subsequent dehydrohalogenation with a base.

Oligomeric polyacids with melting point between 80 and 110°C obtained by reaction of pivalic acid glycidyl ester and trimellitic anhydride have been suggested as curing agents for epoxy resins in powder coatings in a patent of Shell¹⁰¹⁾.

New cross-linker being a caprolactam-blocked adduct of tetramethylxylene diisocyanate and trimethylol propane has been developed and evaluated in powder coatings. Minor advantages compared to the present cross-linkers based on IPDI have been claimed¹⁰². Simple adducts of caprolactame to m-TMXDI has been described as suitable curing agents for powder coatings with a melting point between 115 and 126°C¹⁰³.

A novel amino resin of tetramethoxymethyl glycoluril (TMMGU) has been reported as a cross-linker for powder coatings¹⁰⁴. In addition, sulfonimide catalysts of general formula $\text{RSO}_2\text{NHSO}_2\text{R}'$ have been claimed to be suitable for promoting the curing reaction of hydroxyl functional binders with TMMGU¹⁰⁵.

A novel technique to use liquid cross-linkers in production of powder coatings has been developed. The liquid cross-linkers being alkoxyated melamine resins are adsorbed on porous materials and then processed in the same manner as the other solids. It has been claimed that this technique is a viable alternative to blocked isocyanate for formulating powder coatings based on hydroxyl functional polyester resins¹⁰⁶.

Higgenbottom et al.¹⁰⁷ report the successful use of toluene sulfonamide modified melamine formaldehyde resins as cross-linkers for powder coatings. Contrary to conventional melamine resins which are liquid materials at room temperature with T_g far below zero, toluene sulfonamide modified melamine resins are solids with T_g around 40°C. They claim cured films have excellent solvent and impact resistances. However, blistering problems caused by splitting off of methanol as a by-product of the curing reaction restricts the use of these cross-linkers only to thin layer powder coatings.

β -Hydoxylalkylamides are new class of cross-linkers for powder coatings introduced in 1990 as alternative for TGIC. Pleger¹⁰⁸ claims the following advantages of Primid XL-552 (tertaethanoladipate diamide) over TGIC: low temperature cure, excellent exterior durability, ease of application by tribo charging, nontoxicity, lower costs, and better storage stability of the powder coatings due to higher T_g . However, yellowing resistance is inferior compared to TGIC as well as the tendency to pinhole forming due to water release during curing. Stabilized version of polyester resins improve the yellowing resistance of the film¹⁰⁸. The cross-linker is recommended for formulating powder coatings for metal outdoor furniture, farm equipment, aluminium extrusions, steel and aluminium wheels, transformers, and irrigation pipe and fixtures¹⁰⁹. An advantage of β -hydroxylalkylamides is their nonhazardous nature which has been proven by acute oral and dermal toxicity tests, chronic or subacute toxicity tests, skin and eye irritation tests, skin sensation determinations and mutagenicity evaluations¹⁰⁹. Wood and Hammerton disclose the structure of the only commercially available cross-linker of this type Primid XL-552 (Rohm & Haas Co.) being 85-90% bis (N,N-dihydroxyethyl) adipamide with the most of the remaining material being higher order condensation products of the base material^{110, 111}.

β -Hydroxyethyl adipamide as a cross-linker has been described in a patent of PPG¹¹². The binder is a combination of carboxyl functional acrylic copolymer as a flexibilizer and a polyester resin with a melting point of 95-105°C prepared by esterification of hexanediol with dodecanedicarboxylic acid.

Novel type of cationic curable powder coatings based on vinyl ether functional polyurethanes and crystalline reactive diluents with vinyl ether functionality have been described in a paper of Hilborn et al¹¹³⁾. Improved flow properties have been claimed due to sharp melting at 40 or 60°C and no cross-linking below 120°C, where the latent cationic initiator started to decompose.

4.3. Production and application techniques

A production method for thermoplastic powder coatings to avoid the grinding problems, and in which liquid nitrogen is used during pulverisation, has been described in a patent of Diacel-Huls¹¹⁴⁾. Polyamide powder coating has been produced by hot-melt compounding of a blend of carboxyl- and amino-terminated low molecular weight polyamides and titanium dioxide. After cooling, the compound has been grinded in a simple mill to produce particles with required particle size. The particles have been treated with methanol solution of H_3PO_4 as a polymerisation catalyst, and subjected to solid phase polymerisation under nitrogen at 150°C in order to reach the molecular weight necessary for having good mechanical properties.

A new method for production of powder coatings with special properties has been disclosed in a patent of Duroplast Powder¹¹⁵⁾. The production method is hot-melt compounding in an extruder in a conventional way. When the melt has been discharged from the extruder, a liquid or a liquid/solid mixture of quarternary ammonium salts or their blends with tertiary amines is sprayed onto the melt or the granules formed after cooling. The purpose is to increase the frictional charging or the chemical reactivity of the powder coating.

Flame-spray coating technique which has been developed to allow powder coatings to be applied to practically any substrate has undergone further improvements. Glass and DePoy¹¹⁶⁾ report the latest developments in equipment and polymer design in order to overcome the problems which lead in the past to failures. Advancements are booked in equipment streamlining, nozzle configuration, fuel type versatility, hose lengths, and hopper/feed mechanics. The newly developed resins, being modified ethylene-acrylic acid copolymers, are characterized by random pendant carboxyl-carbonyl functionality, capable of forming ionomeric and hydrogen bonding interactions with polar and ionic sites on blasted metal surfaces. This ensures excellent adhesion to the substrate, minimizing the disbondment problems resulting from thermal cycling and abusive environments.

The use of differential scanning calorimetry (DSC) in investigating the effect of flame spray conditions on crystallinity and mechanical properties of thermoplastic powder coating for flame spray applications has been described by George and Reimer¹¹⁷⁾.

A new equipment for field application of thermoplastic powder coatings has been described¹¹⁸⁾. In the technique which uses hot air heated to temperature higher than the melt point of the resin, the powder particles heated in this way are ejected under pressure from the sprayer to the object to be coated. This alternative to the flame spray technique is claimed to be suitable for application of protective powder coatings on field.

5. Future Trends

Hybrids paints composed of blends of polyacrylic polymer dispersions with different types of polycondensation polymers (alkyds, polyesters, epoxies, polyurethanes) will play an important role in the next generation of water-borne paints. In this way, unique properties can be expected benefiting from the synergistic effect of these different systems.

Cross-linkable polymer dispersions will certainly undergo further developments. Creating a network by additional cross-linking of the thermoplastic polymers gives a possibility to overcome the typical problems that the paint people are confronted when working with thermoplasts with inferior solvent and chemical resistances, low blocking, and dirt pick-up resistance.

It can be expected that in the years to come, alkyd emulsions will play an important role as binders for environmentally friendly paints for architectural application. They offer in principle formulation of zero-VOC paints, enjoying the benefits of the traditional alkyd-based coating.

Dispersing of the pigments in water-borne coatings is a problem which has to be approached in somewhat different way compared to the conventional solvent based systems. The pigment dispersants of nowadays belong commonly to the well known surfactants. New developments should be expected in block copolymers as dispersing agents for water-borne coatings.

Gradual increase of the solids content in high-solids coatings can be expected by improvement of the synthetic methods to obtain polymers with narrower molecular weight distribution. In this way the solid content can be improved without affecting adversely overall properties of the coating by reducing molecular weight.

Development of nontoxic reactive diluents for one- or two-component high-solids coatings remains an attractive route for reaching the ultimate goal of having 100% solvent-free liquid coatings.

Hyperbranched polymers which are characterised with unique properties, among the other low viscosity at high molecular weight, can be another approach to create high-solids coatings which will not suffer from lack of mechanical properties due to the use of low molecular weight binders. However, the synthetic methods for these polymers described in the literature are still not suitable for commercial production.

In order to improve flow properties of powder coatings, more emphasis will be given to synthetic routes for producing polymers with better-defined structure compared to the nowadays polymers obtained by irregular statistical linking of the monomer-building blocks. This will lead to narrow molecular weight distributions of the polymers with desired position of the reactive groups available for additional cross-linking.

Higher penetration of the computers in the resin and paint laboratories together with the numerous programs and models simulating the molecular weight build-up during synthesis of the polymers and during the cross-linking process. Systems with improved overall properties can be expected as a normal consequence of the use of these contemporary tools in the development work.

The permanent search for cross-linkers with lower or no toxicity will certainly lead to development of new cross-linking systems which will differ from the well established epoxy/carboxyl and hydroxyl/isocyanate of nowadays. Another driving force in looking for new cross-linking mechanism is certainly the desire to lower the curing temperatures not that much because of energy savings, but more as a prerequisite to enter new markets such as wood or plastics.

There is a clear trend towards thinner films. The common film thickness of powder coatings of nowadays is ca. 50 μm . It is expected that a layer thickness of 20–30 μm in a near future can be a realistic target. However, it must be emphasized that the full success in realizing this depends on factors being outside of the control of the powder-paint producer, such as type and pretreatment of the substrate, application equipment and oven heating rate, as well as factors which can be kept under control by the paint producer such as particle-size distribution, polymer selection, rheology control, etc.

Powder coatings for precoated metal are probably successors of various types of conventional coil-coated materials. Therefore, a new generation of powder coatings withstanding the postforming treatment should be an expected development.

Present TGIC powder coatings are suitable for outdoor application with 15–20 year service life. PVDF powder coatings are even with higher outdoor durability. In order to compete with the superior brothers, polyester powder coatings will probably undergo further improvements with respect to the outdoor durability.

Stevenson¹¹⁹⁾ predicts revival of the thermoplastic powder coatings in the near future. His predictions are based on the new achievements in powder coatings with small particle size, thus improving flow properties, and combination of properties by blending of different polymers such as poly(vinylidene fluoride) (PVDF) with poly(methyl methacrylate) (PMMA), or nylon with PVDF.

Powder-coating primer surfacer with excellent chip resistance is applied on commercial scale by Chrysler in Dodge City for pick-up cars. The complete system is consisted of electrocoat of 30 μm , epoxy/polyester primer surfacer with a film thickness of 50–80 μm with conventional wet coating as a top layer. It is to expect that automotive primer surfacer will be the earliest great success of powder coatings in the automotive sector.

Automotive clear coat remains the most attractive target for powder-paint producers. Problems to be solved in the future are : powder stability, incompatibility with other powder paints, and price with respect to the layer thickness which is still a high obstacle from very practical reasons. Minimum film thickness allowing acceptable flow has to be reduced to at least 60 μm compared to 100 μm , which can be considered as present state of the art. Powder stability during the recycling and improved transfer efficiency (from 60% to at least 80%) are also items of improvement.

Lattke from BMW¹²⁰⁾ states that with powder clear coat, only 13% solvent reduction can be obtained. In his opinion, this is relatively small reduction to be as such a driving force to introduce a fully new system in the automotive industry. This should be combined with other advantages in order to expect acceptance by the market, since the quality demands will never be lowered because of environmental pressure.

Metal has been always a substrate for application of powder coatings. As a result of the environmental pressure, it is to expect that powder coatings will penetrate in the future in the wood-furniture market. However, enormously big conceptual changes have to take place before powder paints touch the area of heat-sensitive substrates.

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