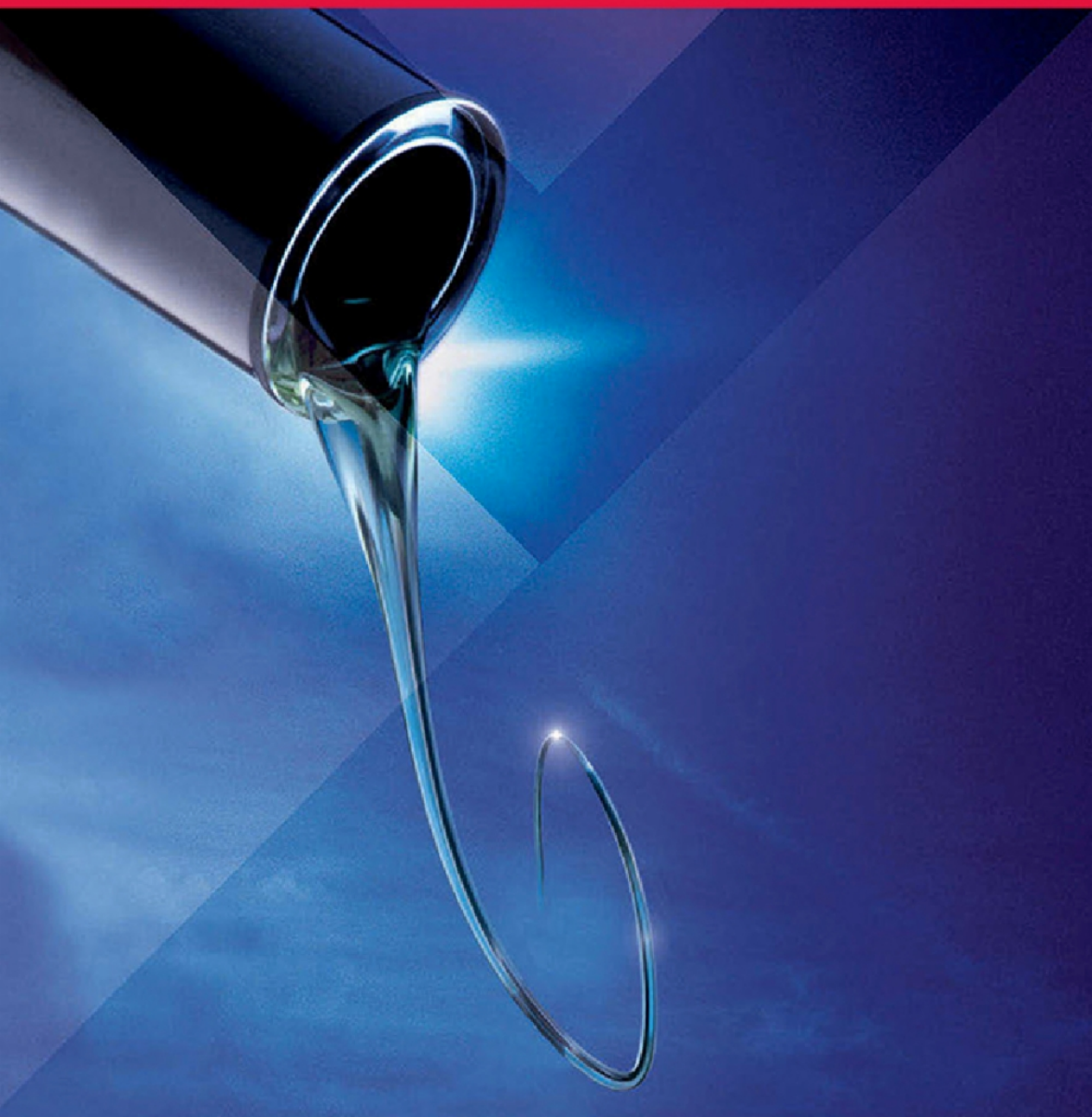


EUROPEAN COATINGS TECH FILES



U. Poth | R. Schwalm | M. Schwartz

Acrylic Resins



Vincentz Network GmbH & Co. KG

Ulrich Poth | Reinhold Schwalm | Manfred Schwartz

Acrylic Resins

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Preface

Acrylic polymers are essential products for various industrial application fields. Particularly, they play important roles as binders (acrylic resins), dispersion resins and polymer thickeners in the coatings industry.

Since acrylic resins were launched onto the coatings market, they have distinguished themselves by meeting various quality requirements and replacing other resins. Acrylic resins are used in eco-friendly coating systems, for example. Thanks to their broad range of properties and to ongoing developments within this product class, they also serve as ingredients for many different coating systems.

The present book presents an overview of the production, properties and application of acrylic resins and their distinctive features. It covers acrylic resins prepared by solution polymerization and emulsion polymerization, as well as reactive acrylic resins which form films by radiation curing. Besides a general description of these three product classes, there are chapters dealing with particular properties for the diverse application fields.

The goal of the book is to convey the latest knowledge about acrylic resins in solvent-borne and water-borne systems, and for radiation curing in an understandable and descriptive manner. Given the breadth of applications for acrylic resins, the book discusses the different chemical and physical aspects of the production methods and the related application properties. There are numerous literature citations for further reading on specific issues.

The book is aimed at students and newcomers to the field of coatings technology, and also at well-versed experts in coatings applications and other related industries. The essential background information herein will underpin decisions concerning the choice and use of acrylic resins.

Münster, Ludwigshafen, São Paulo, March 2011

Ulrich Poth Dr. Reinhold Schwalm Dr. Manfred Schwartz

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In reality, methyl iso-butyl ketone emerges as the best solvent from the study as it combines high regulating efficiency and thinning behaviour. For that reason, for a long time in the U.S.A., ketones were preferred for process solvents and for paint formulations. However, they could not be used on the European market because customers rejected their pronounced ketone odour. In the meanwhile, some α -ketones are suspected of being harmful to health and are being replaced by other solvents.

3.5 Types, properties and application of acrylic resins

The biggest field of application for acrylic resins made by solution polymerization is solvent-borne paints, of course. However, products made by solution polymerization also lend themselves to the production of water-borne secondary acrylic dispersions and powder coatings.

3.5.1 Acrylic resins for solvent-borne coatings

Solvent-borne coatings based on acrylic resins are nearly exclusively used in paints that form films by crosslinking. The most important crosslinking reactions are those of methylol acrylamides (self-crosslinking) and the reaction between hydroxyl groups and amino resins or polyisocyanates that contain free or blocked isocyanate groups. Other crosslinking reactions have so far played a minor role.

When acrylic resins were first developed, the resin solutions were used to make paints that dry solely physically (thermoplastic acrylic resins, TPAs). Nowadays, such products are only used in special cases.

3.5.1.1 Thermoplastic acrylic resins

From the mid-1920s on, industrial coatings were predominantly formulated with a cellulose nitrate binder, which was combined with plasticizers or, later, with alkyd resins. These paints were distinguished by ease of application, fast physical drying at ambient temperatures and good pigment loading (high brilliance). Their disadvantages included poor weatherability, a tendency to yellow, and relatively low resistance to solvents and chemicals. The mid-1930s saw the launch of stoving enamels for automotive OEM paints, which were based on alkyd and amino resins and which confer much better resistance. In the 1940th were developedth thermoplastic acrylic resins for coatings that form films at ambient temperatures.

These can be produced by both solution and suspension polymerization. The products mainly contain methyl methacrylate, or its combination with other methacrylic esters for adjusting the glass transition temperature. The paints may also contain plasticizers; they dry by physical means only. They are notable for rapid initial drying at ambient temperatures, relatively good weatherability, and do not yellow. On account of those properties, thermoplastic acrylic resins were used for automotive repair finishes, mainly in the U.S.A. However, these failed to match the application properties of cellulose nitrate combinations, or their high pigment loading (brilliance). Thermoplastic acrylic resins are therefore mainly used for physically drying clear coats.

A further disadvantage is that coatings based on simple thermoplastic acrylic resins do not adhere very well on metal surfaces. Much better adhesion on metal results from modifying such acrylic polymers with certain amounts of methacrylic acid or, even better, with aminoalkyl acrylic esters (see Chapter 2.2.3.3), methacrylamide or methacrylonitrile^[13]. Paints containing such copolymers are used for metal coatings, even for can-coatings, e.g. adhesion coatings for crown caps.

Another field of application for thermoplastic acrylic resins is impregnation of mineral substrates. They serve here as a primer sealer for concrete and plastered masonry, prior to application of the wall paints.

Thermoplastic acrylic resins also form the basis for strippable varnishes, which provide temporary protection for metal surfaces.

In addition, such acrylic resins find application in the coating of paper (e.g. overprint varnishes), plastic parts and leather.

Furthermore, it has also been recommended that acrylic resins containing methacrylic esters with long side-chains be added to alkyd paints to accelerate their initial drying velocity.

Currently, the most serious disadvantage of all the products described here is the low solids content of the resultant paints. Thermoplastic acrylic resins yield acceptable properties in terms of drying rate, adhesion, flexibility and relative resistance only if they have high molecular masses and high glass transition temperatures. The average molecular masses of the resins are between 30,000 and 100,000g/mol; the glass transition temperatures are between 60 and 95°C. Both properties lead to relatively high solution viscosities respectively low application solids. Clear coats containing such resins have application solids of 20 to 25 wt.%, and do no longer meet the requirements of VOC regulations. They must therefore be replaced by water-borne systems or by coatings based on resins which form films by crosslinking and which have much higher application solids.

Examples of commercial products: Plexisol (Röhm GmbH), Paraloid F (Rohm & Haas – Dow), Neocryl (DSM), Viacryl types (Cytec-Vianova), Synocryl types (Cray Valley)

Numerous products are made by suspension polymerization. They have the same properties and application fields as those made by solution polymerization. Acrylic resins made by suspension polymerization have broader molecular mass distributions (see Chapter 2.3.2).

Examples of commercial products: Neocryl B grades (DSM)

On account of their low glass transition temperatures, acrylic resins which contain just acrylic esters are termed “soft” resins. For example, poly-n-butyl acrylate is a liquid, although the polymer has a high molecular mass. Such resins are unsuitable as the sole binders for paints, but they do serve as additive resins, e.g. as polymer plasticizers.

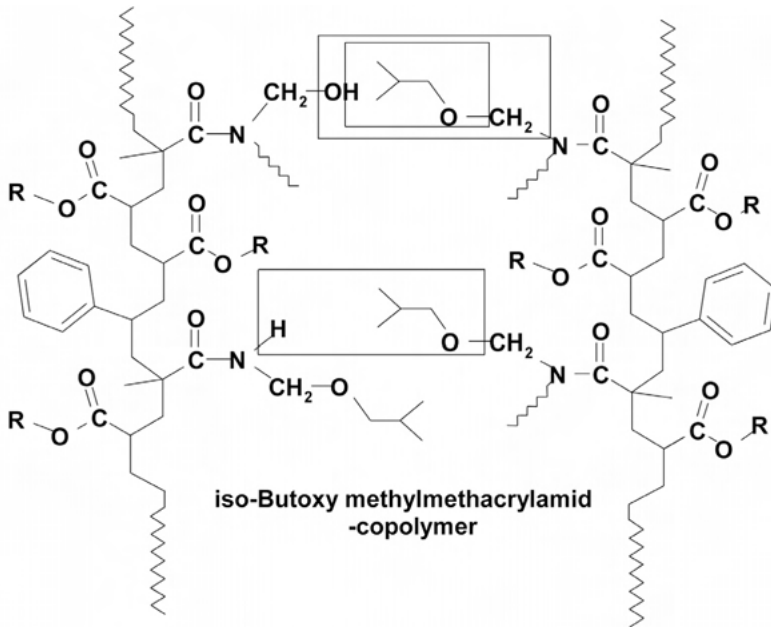
Examples of commercial products: Acronal L types (BASF SE)

3.5.1.2 Acrylic resins with methylol acrylamides

As far back as the early 1940s, it was known that acrylic resins made from acrylamide or methacrylamide are water-soluble polymers that can be crosslinked by adding formaldehyde^[15]. Back then, they were used for plastic parts. The 1950s saw the advent of coating resins which actually utilised this crosslinking mechanism. Initially, copolymers were made from acrylamide or methacrylamide (or blends thereof), which were then methylated with formaldehyde^[16]. The resultant methylol ethers are unstable, and react with each other at ambient temperatures. Therefore, just like the amino resins, the process was modified so that the methylol ethers were etherified with mono-alcohols^[17]. These alcohols were primarily butanols, which already being used as process solvents. The resultant acrylic resin contains butoxymethyl (meth)acrylamide by way of monomer unit (see Chapter 2.2.3.4). Later, the complex monomer as such was made separately by reaction of acrylamide or methacrylamide with the semi-formal of butanol, and then copolymerized with other monomers in solution to yield acrylic resins. The first (meth)acrylamide polymers were water-soluble, whereas the newer resin class consists of combination monomers and comonomers which are relatively hydrophobic. The process solvents were mixtures of aromatic hydrocarbons (e.g. xylene) and butanols (e.g. n-butanol).

Acrylic resins containing alkoxymethyl acrylamides as building blocks can crosslink by themselves.

In the earlier literature, and down to this day, the first reaction is believed to involve a reaction between methylol ether and etherified methylol ether, with cleavage of water or alcohol. By analogy with the reaction of amino resins, here it is assumed that the crosslinking reaction starts at the imino groups, which then react with methylol ethers and etherified methylol ethers to form methylene bridges. However, the methylol ethers subsequently participate in crosslinking reactions among themselves and finally – depending on the crosslinking conditions – formaldehyde is cleaved (see Formula 3.7).



Formula 3.7: Crosslinking reactions of alkoxymethyl (meth)acrylamide copolymers

The crosslinking is carried out at temperatures of 150 to 180°C and can be accelerated with acid catalysts. However, there is no need to add acid catalysts if the acrylic resins already contain sufficient quantities of acrylic acid or methacrylic acid, generating acid values of 30 to 40mg KOH/g.

In a manner similar to the reaction of amino resins, the carboxyl groups do not really participate in the crosslinking process, despite what has been stated in the literature for a long time.

On the other hand, it is possible to copolymerize hydroxy-functional monomers into the acrylic resins. The hydroxyl groups react with alkoxymethyl (meth)acrylamides forming methylol ether bridges, with release of monoalcohols.

Alkoxymethyl (meth)acrylamides form films by self-crosslinking and are notable for their excellent adhesion on metal and outstanding chemical and solvent resistance. Their high chemical resistance – to acids, as well – is an indication that the molecular network of such coating films mainly contains methylene groups. Where resins additionally contain hydroxyl groups that form methylene ether bridges, the chemical resistance of such films is relatively moderate.

The attainable properties predestine such paint systems for the production of can coatings. These offer excellent resistance to all kinds of filling goods. For example, can coatings are tested by treatment with boiling lactic acid (sterilisation tests).

As the resistance to alkali and surfactants is excellent, coating systems based on alkoxymethyl (meth)acrylamide copolymers are ideal for domestic appliances, mainly for coatings for washing machines and refrigerators (“white goods”). A typical coating for washing machines is a white, one-layer coat based on an alkoxymethyl (meth)acrylamide copolymer. A disadvantage of such lacquers has been the relatively high solvent content. For example, a white-pigmented, one-layer coat would have had application solids of just 40 to 50 wt.%. This triggered the development and market launch of resins with lower molecular masses. Ultimately, though, this class of product was replaced. Currently, coating systems for so-called “white goods” are powder coatings based on aromatic epoxy resins and crosslinked by carboxyl groups (carboxylic acids and derivatives, carboxy-functional polyesters).

Examples of commercial products: Synthalat A 600, A 645 (Synthopol Chemie), Uracron CS types (DSM), Viacryl SC types (Cyttec-Vianova), Synocryl 836, 839 (Cray Valley)

3.5.1.3 Hydroxy-functional acrylic resins crosslinked by amino resins

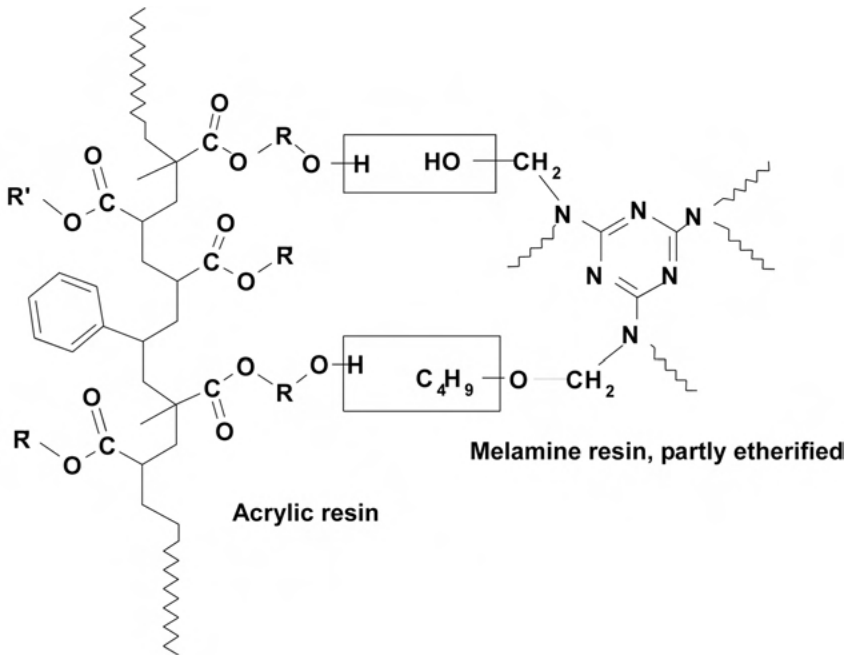
Surprisingly, it was not until the 1950s that combination resins for amino resins not only played a plasticizing role, but could also react by crosslinking (co-crosslinking) with free hydroxyl groups present on the functional groups of amino resins. First, the preferred resins were hydroxy-functional alkyd resins. The late 1950s saw the advent of the industrial production of hydroxy-functional acrylic monomers by making acrylic acid or methacrylic acid react with ethylene oxide and

propylene oxide^[18]. Numerous copolymers produced from such hydroxy-functional monomers and other acrylic or methacrylic esters, along with other comonomers, were developed in the 1960s and evolved into the most important class of resins, namely solution polymerization products.

Characterization of hydroxy-functional acrylic resins

First of all, hydroxy-functional acrylic resins are combined with amino resins as crosslinkers. The functional groups (methylol and methylol ether groups) on the amino resins react with the hydroxyl groups on the acrylic resins.

The reactions take place at elevated temperatures. Efficient crosslinking temperatures vary with the type of amino resin from 125 to 200°C, and the reactions may be catalysed by acids.



Formula 3.8: Crosslinking reactions of hydroxy-functional acrylic resins and melamine resins

Note: This is a model representation of an acrylic resin, which is repeated deliberately in the following formulas. Other compositions are conceivable.

The effective crosslinking conditions can be lowered to ambient temperatures by adding sufficient amounts strong acid (e.g. hydrochloric acid). Adding smaller quantities of organic acids (e.g. p-toluenesulphonic acid) lowers the effective crosslinking temperature for hydroxy-functional acrylic resin with a typical amino resin from 130°C to 80°C. This is important where heat-sensitive substrates (e.g. plastic parts) have to be coated. In addition, so-called internal acid catalysis exerts an influence. Hydroxy-functional acrylic resins always contain small quantities of carboxyl groups. These stem from small fractions of residual free acids from the industrial monomer-production process. However, hydroxy-functional acrylic resins are deliberately formulated with specific admixtures of free acid monomers whose purpose is to catalytically influence crosslinking with amino resins. Adequate storage stability of such paint systems is achieved by adding added mono-alcohols to act as solvents. The alcohols shift the equilibrium towards the reactants. For the same reason, salts of such acids with volatile amines are used instead of free acid catalysts.

Amino resins available for crosslinking are urea resins, melamine resins, benzoguanamine resins, and some of the carbamate resins. The most important crosslinkers for hydroxy-functional acrylic resins are the melamine resins on account of their weatherability, which dovetails well with the properties of acrylic resins. Formula 3.8 shows the possible crosslinking reactions between hydroxy-functional acrylic resins and melamine resins.

All amino resins – and hence melamine resins, too – undergo self-crosslinking. The relative extents of co-crosslinking and self-crosslinking influence the film properties significantly. Co-crosslinking confers flexibility, weatherability, and chemical resistance. By contrast, self-crosslinking boosts physical hardness, gloss, and solvent resistance. Principally, both types of reaction occur in parallel. However, it is possible to influence the extents of the different crosslinking reactions. Co-crosslinking is increased by having higher proportions of acrylic resin than melamine resin, higher proportions of hydroxyl groups, highly reactive hydroxyl groups, the use of less reactive melamine resins, less acid catalysis, lower crosslinking temperatures, and longer reaction times (effect of film-forming conditions).

Conversely, self-crosslinking reaction is increased by higher proportions of melamine resin, stronger acid catalysis, higher stoving temperatures, and short reaction times.

Typical acrylic resins for crosslinking with melamine resins have number-average molecular masses of 3000 to 8000g/mol; hydroxyl values of 60 to 130mg KOH/g, i.e. 5.3 to 11.6 hydroxyl groups per resin molecule (number-average molecular mass of 5000g/mol), and acid values of 10 to 25mg KOH/g. The preferred glass transition temperatures are between -10 and 50°C . The delivery form is 50 to 70%, dissolved in aromatic hydrocarbons (e.g. xylene, Aromatic 100), sometimes in combination with some more-polar solvents (e.g. butanols). Table 3.1 shows a typical example of hydroxy-functional acrylic resin for crosslinking with melamine resins in stoving enamels.

Table 3.1: Typical acrylic resin for crosslinking with melamine resins

Ingredients	wt. %
Xylene	37.3
Charge, heat to 140°C , hold temperature	
2-Hydroxypropyl methacrylate	15.4
Methacrylic acid	1.2
2-Ethylhexyl acrylate	40.0
Methyl methacrylate	23.5
N-Butyl methacrylate	19.9
Total monomers	100.0
Mix, add over 4h	
Di-tert.-butyl peroxide	1.0
Xylene	4.0
Mix, add in parallel, then hold for 0.5h	
Di-tert.-butyl peroxide	0.4
Xylene	2.0
Mix, add, hold for 2h, then cool down	
Total	144.7
Characteristics: NV (60° – 130°C): 69.6% acid value (NV): 9.8mg KOH/g viscosity (50% in xylene) 560mPa s	

These types of acrylic resins are used for stoving enamels for industrial appliances (machines and equipment) and primarily for automotive OEM finishes, mainly topcoats, base coats and clear coats^[20].

Examples of commercial products: Lioptal A types (Synthopol Chemie) Setalux (Nuplex), Synthacryl (Cytec Vianova), Uracron CR types (DSM), Synocryl types (Cray Valley)

Since the 1970s, various restrictions have been imposed on the emission of solvents during paint application. First, solvents were evaluated on the basis of their photolytic effects and their use was correspondingly restricted.

This spurred the development of so-called **NAD acrylic resins** (non-aqueous dispersions), initially in the U.S.A. Then followed measures and regulations aimed at reducing solvent quantities generally. There were various reasons for this: less use of products which are dependent on mineral oils, environmental protection, and health considerations. This led to the development of **high-solid resins**, later to **water-borne systems**, and finally to **powder coatings** based on acrylic resins.

NAD acrylic resins

At the end of the 1960s, analysis in the U.S.A. showed that photolytic compounds support smog formation and deplete the ozone layer. They led to regulations aimed at avoiding such compounds. The compounds in question were halogenated hydrocarbons and aromatic hydrocarbons. One part of the regulation was a ban on the use of chlorofluorohydrocarbons as cooling fluids in all kinds of cooling equipments. Coatings were affected on account of their content of aromatic hydrocarbons as solvents. At that time, there were no restrictions on the use of other solvents, e.g. esters, alcohols, aliphatic hydrocarbons, or ketones. Nowadays, but for different reasons, there are restrictions on the use of aromatic hydrocarbons as solvents in Europe, too. Some of the solvents are classified as toxic, are prohibited and are no longer used in paint systems: benzene and toluene. Other aromatic solvents are defined as harmful to health, and there are specific restrictions on the quantities which may be used in formulations: xylene, ethylbenzene, cumene, and 1,2,4-trimethylbenzene.

Until today, aliphatic hydrocarbons (white spirits) are considered to have only a minimum of healthy risks. However, aliphatic hydrocarbons are unsuitable for acrylic resin solutions, which require more-polar solvents to form stable solutions. Therefore acrylic resins were developed which form stable dispersions in aliphatic hydrocarbons. To differentiate them from the widely known aqueous dispersions, they are called non-aqueous dispersions (NAD). They are prepared in different ways, some of which are described below.

As in aqueous dispersions, stabilization of non-aqueous dispersions is warranted by surfactants and protective colloids. Various stabilizers are soluble in aliphatic hydrocarbons, as well as being compatible with hydroxy-functional acrylic resins.

There are polycaprolactones, which are prepared from ϵ -caprolactone, opened by water and formed in a polyaddition reaction. The carboxyl group on the one end of this polymer is made to react with glycidyl methacrylate, yielding macro-monomers which are soluble in aliphatic hydrocarbons. Specific quantities of these macro-monomers are copolymerized in aliphatic hydrocarbons (white spirit) together with essentially more-polar monomers.

The macro-monomers become oriented on the surface of particles and carry and stabilize these particles in the non-polar solvent^[22].

Other carriers are prepared by making hexahydrophthalic anhydride react with the glycidyl ester of neodecanoic acid. The resultant terminal carboxyl groups are made to react with glycidyl methacrylate as well. The ensuing non-polar soluble macro-monomer is also incorporated into a copolymer to form a stable dispersion in aliphatic hydrocarbons^[23].

In other processes, non-soluble seed polymers are made in aliphatic hydrocarbons. Non-polar monomers are then added to the polymerization process, yielding more soluble shells and finally a stable, non-aqueous dispersion^[24].

Another advantage accrues from using NADs, apart from the fact that a less-hazardous aliphatic hydrocarbon is involved. The viscosity behaviour of all polymer dispersions differs from that of organic solutions. To an extent depending on their solids content, they can have much steeper viscosity curves. Consequently, low viscosities are achieved at lower thinning rates. Paints based on non-aqueous dispersions therefore have relatively higher solids content at application viscosity

than those based on comparable hydroxy-functional acrylic resins in organic solutions. Figure 3.5 shows such a comparison of viscosities.

Film formation of paints based on acrylic-based NADs takes place by evaporation of solvents and fusion of the dispersion particles, mostly at elevated temperatures (stoving enamels). The efficiency of film formation may be supported by adding high-boiling polar solvents. After the aliphatic hydrocarbons have evaporated, the high-boiling polar solvents form true solutions with the resins until they evaporate as well.

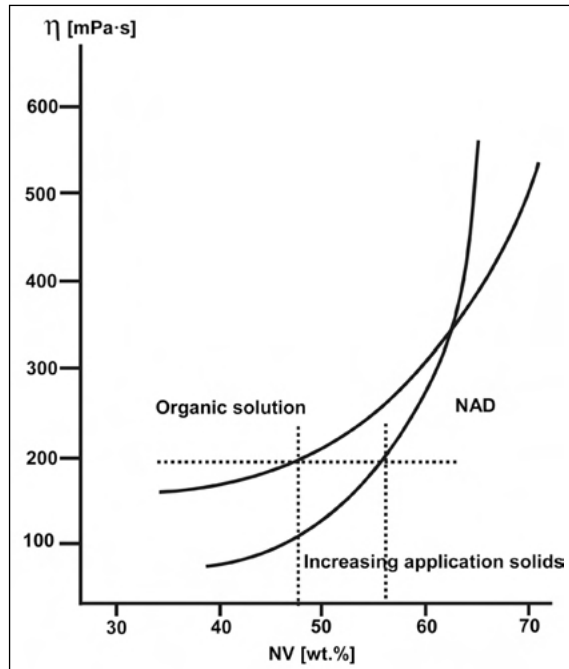


Figure 3.5: Comparison of viscosities of NAD and an organic solution of acrylic resin

The preparation of an aqueous dispersion of crosslinked acrylic polymers (microgels) by emulsion polymerization constitutes a special process. The aqueous dispersion is transferred into a non-aqueous dispersion by adding solvents and extra resins; the water is separated and removed^[25]. Because the particles are crosslinked, they are insoluble in organic solvents, and the added resins act as protective colloids for the polymer. As the particles are swellable in organic solvents, they confer pseudoplastic viscosity behaviour by virtue of particle-particle interaction. Where films undergo physical drying, the particles generate increasing levels of viscosity. This prevents the films from sagging on vertical surfaces. Due to this property, NAD microgels have a stabilizing effect on the orientation of flake-like pigments, e.g. aluminium pigments, and support formation of the metallic effect in solvent-borne automotive base coats, even when the base coats have relatively high application solids.

High-solid acrylic resins

Ongoing requirements aimed at reducing solvent emissions during paint application spawned the development of formulations with higher application solids. For example, high-solid contents of spray-paints are required at application viscosity of about 25" to 35", measured as flow-out viscosity (DIN 53211, 4 mm flow cup, at 23°C), corresponding to 85" to 110" (ISO 2431, 4 mm flow cup, at 23°C), or 120 to 180mPa s in a rotation viscometer at the same temperature.

Among others, the viscosity of paints depends on the viscosity of the polymer solutions (resins in the formulation). The latter varies with the polymer concentration (in this case, it should be as high as possible), the temperature, and the average molecular mass and molecular mass distribution of the polymer, the solubility of the polymer and the solvent power of the solvent. The first step to achieve these requirements was to reduce the average molecular masses of polymers. For acrylic resins, this means choosing those process conditions – the various influences are described above (see Chapter 3.3.3) – which are conducive to low molecular masses, and hence a low viscosity, thereby opening up the chance to increase the application solids. To achieve hydroxy-functional acrylic resins of lower molecular mass, a higher initiator concentration and higher polymerization temperatures are chosen. Prolonging the feed time has little effect. And, using large quantities of solvent for the polymerization contradicts the goal of achieving the highest-possible solids content.

However, lowering the molecular mass of acrylic resins does impair some coatings properties. The step from a resin molecule of low-molecular mass to crosslinked molecules of infinite molecular size by chemical film formation is much larger than it is when going from conventional resins. It is therefore