H. Warson and C. A. Finch

APPLICATIONS OF SYNTHETIC RESIN LATICES

Volume 1

Fundamental Chemistry of Latices and Applications in Adhesives

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by
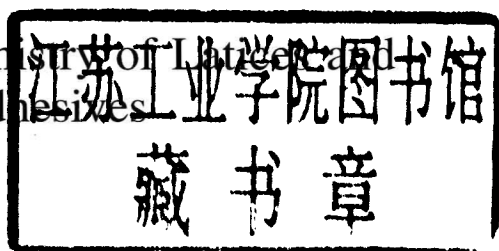
H. WARSON
Chemical Consultant, UK

and

C.A. FINCH
Pentafin Associates, UK

Applications of Synthetic Resin Latices
Volume 1

Preface

A word, allow us, sweet ladies and gentlemen
We pray you hear, while we alone appear,
We are the Prologue

In 1972 a volume by one of the current authors appeared under the title *Applications of Synthetic Resin Emulsions*. This has long been out of print. The many advances that have been made, both in the development of polymer emulsions (described more correctly as latices, by analogy with natural rubber latices) and their application in various industries, merit a new trilogy under the title *Applications of Synthetic Resin Latices*. In the words of the slightly modified quotation from an English version of the Prologue to Pagliacci, which was quoted in the Prologue to the earlier book, the current volumes are still the only comprehensive ones on the subject.

With the present trends in ensuring environmental safety, water-based latices are having an ever-increasing role in a diverse range of applications. Many of these overcome the limitations of water-based polymers since in film forming a minimum temperature is necessary. In the case of some polymers, there are limitations due to insufficient film hardness, with a tendency of films to 'creep' on a vertical surface.

Developments in the formation of latices have included increasing molecular weights of polymers and the use of 'core–shell' copolymers, which often have the effect of reducing the minimum film-forming temperature, therefore enabling harder films to be formed and, above all, the use of crosslinking reactions, often described as 'curing'. As this has now become a major part of the technology of the preparation and application of these latices, it is the subject of a separate chapter. The minimum use of water-soluble emulsion stabilisers, or in some cases the use of stabilisers that can become water insoluble, is another feature of developments in latex technology.

The general structure of these volumes is similar to that of the earlier book. Each chapter is complete in itself, but a limited amount of repetition occurs between the earlier chapters, which describe the chemical basis of the processes and also additives required in applications, e.g. pigments as well as some typical commercial products, and the specific chapters on the various application industries.

Like the previous text, these volumes are intended for three classes of readers: chemists and other scientists who are performing the necessary research and development, technical service personnel who examine latices for potential applications and also, not least, the technologists in the application industries who may wish to use these water-based systems.

The standardization of units and their presentation has caused some problems, particularly with the adoption of the various SI units. The hybrid units sometimes found in patent applications have been avoided as far as possible, e.g. pressures in pounds per square centimetre and area dimensions given in square inches but with the thickness in millimetres. Temperatures are normally quoted in degrees Celsius (°C) but exceptionally in degrees Fahrenheit (°F), especially when results were originally quoted in rounded figures such as 250 °F and 300 °F. In most cases, however, units quoted in papers and patents are quoted as in the originals.

Sufficient information on technology is included for the processes involved to be understood, but no pretence is made that the chapters concerned provide comprehensive expertise on a wide range of industries. It is to be hoped that the texts will also point the way to future improvements and that these volumes, produced at the start of the new century, will be useful for many years to come.

Henry Warson
26 Blythe Court, 4 Grange Road,
Solihull B91 1BL

C.A. Finch
18 West End,
Weston Turville,
Aylesbury HP22 5TT

Applications—A note on References

Austral. P = Australia Patent
BP = British Patent
Belg. P = Belgium Patent
Can. P = Canadian Patent
Cz. P = Czech Patent
East G. P = East German Patent
Eur. P = European Patent
FP = French Patent
GP = German Patent
Ind. P = Indian Patent
Neth. P = Netherland Patent
Pol. P = Polish Patent
Rom. P = Romania Patent
S. Afr. P = South African Patent
Sp. P = Spanish Patent
USP = United States Patent
USSRP = Soviet Union Patent

There is a complication in references to Japanese specifications (JP). From about 1977 all references quoted are to the Japan Kokai, patents which are published before examination. Earlier references may be to the Kokai series or to full patents. These numbers do not correspond in the Japanese system, and if copies are required of earlier patents, it is necessary to check for the required series. The appropriate *Index Volume to Chemical Abstracts* is useful for this purpose.

Patent Validity

Patents are often published in countries other than that in which the original application is applied; hence the country of the patentee may be different from that of the named country. European and World order patents are valid in a number of countries, as indicated in the specifications. In many countries, e.g. Great Britain, France and Germany, patents are now published without examination unless the applicant requires this. It is up to anyone objecting to do so formally, but objection can only be made by a person or persons directly affected by the publication.

Publication of extracts from, or abstracts of, patents in these volumes must not be construed as an invitation to operate them, where the use is protected by laws of the country involved.

Introduction

1 SCOPE

With the growth of the synthetic resin (polymer) industry in the past five decades, a considerable amount of technology has been compiled. Whilst there are many general and specialised volumes dealing both with the chemistry of polymers and their technological applications, we believe that the only single volume which endeavoured to co-ordinate the literature on applications of polymers in emulsion form was that published by one of the current authors in 1972. After nearly 30 years, with the vast increase in available information, it has been found necessary to publish a new compilation in three volumes.

Whilst the terms *resin* and *polymer* do not have exactly the same meaning, they are often used as synonyms where no confusion is likely to occur. Most of the materials with which these volumes are concerned are more properly described as polymers–a general term applied to compounds of high molecular weight featuring substantially repeating units without loss of simple units such as water or ammonia by condensation. This definition applies to vinyl polymers generally, and often, also, to polyepoxides and to polyurethanes. The term resin implies a condensation product of comparatively low molecular weight. As an example of this, apart from uncured aminoplasts and phenoplasts, the term resin is also used to describe products such as the condensates of rosin (of natural origin, usually from trees) with maleic anhydride. A further term, *macromolecule*, is more generally applied to both resins and polymers, but its use tends to be restricted to academic and 'pure' scientific publications. In this text, the terms *polymer emulsion* and *polymer latex* have been used interchangeably throughout, usually depending on the source of the information discussed. The term *latex* is often restricted to rubbers, either natural or synthetic. In the United States, the term *latex* is almost universal, and, indeed, may be considered as more correct. Many products developed in Germany are referred to as *dispersions ('dispersionen')*, so this term is retained in some cases. A *dispersion* may also imply a stabilised solid of a fine particle size often a pigment) in a liquid. However, the term *dispersion polymerization* is applied both to suspension polymerization in aqueous media, and *dispersion polymer* to stabilized macromolecular emulsions in non-aqueous media.

There is no rigid distinction between the properties of a rubber and a resin or polymer. Nevertheless, since rubber latices form a technology of their own, they are not considered here, unless they are proposed as functional alternatives to polymers with more 'plastic' properties. For this reason, the applications of only a limited number of polymers of butadiene, styrene and isoprene are discussed.

It must be admitted that this nomenclature is rather confusing, but, since it will be encountered elsewhere, distinction is made is made between the various terms only where it occurs in technical practice. Otherwise, as long as no ambiguity is likely to be caused, the terms *resin* and *polymer* are used virtually as synonyms.

In nearly every case, the feature of a polymer emulsion is that it is applied as an auxiliary factor rather than as a primary material e.g. it is a medium for a paint, or a major (functional) component of an adhesive. As such, latices have tended, in some ways, to be the 'Cinderella' of the world of polymer science, especially as progress in their applications has been evolutionary, rather than taking place in 'quantum style' leaps.

Information on the preparation, and properties of latices is found in numerous patents, theoretical papers and the literature of the principal manufacturers of monomers and other raw materials. Information on applications of latices is often found in patents and the technical literature of polymer manufacturers. The preparation of a group of latices and their application is often described in the same patent specification. Selected information from these sources is presented in each of these volumes. Some technical journals contain useful data, and much information of considerable technical value is scatter throughout the trade literature, but is seldom abstracted adequately and is often issued undated.

This first volume surveys the fundamentals of polymer chemistry, the principles and practice of polymer latices, including pigmented systems and some current technical latices. The properties of alkali-soluble latices are considered. Volumes 2 and 3 describe in some detail the numerous applications of latices.

Crosslinking and curing of polymers has become important in the last few decades, and is the subject of Chapter 5. Some non-vinyl latices, such as those from alkyds and polyurethanes are also the subject of a separate Chapter, since these have assumed some industrial importance.

2 HISTORICAL AND GENERAL SURVEY

Natural rubber latex has been known in the West since 1736, when it was first introduced to Europe by de la Condamine. Rubber latex is a milky white liquid obtained from *Hevea braziliensis*. This was coagulated, and the product sold as *gutta percha*. After seeds of this tree had been smuggled out of Brazil and propagated in the UK, large scale cultivation commenced

after 1900 in Malaysia, Natural rubber is an example of a natural polymer. It is now known to be a polymer of isoprene, $CH_2:C(CH_3).CH:CH_2$, and may be written in a simple manner as $(C_5H_8)_n$. Its biosynthesis is not from isoprene, but by a complex route through isopentenyl pyrophosphate $CH_3.C(:CH_2)_2.O.P(:O)(OH).O.P(:O)(OH)_2$ [1]. It is necessary to consider the term latex in greater depth. A latex is a special case of an emulsion, which is a special case of a suspension of an insoluble liquid or 'oil' in water prepared so that it is stable for long periods, of the order of months or, even, years, rather than minutes. To ensure that an emulsion remains stable, and that the two phases do not separate, it is necessary to add suitable emulsifying agents, alone or in combination (see Chapter 2) These emulsifiers function by their surface activity at the interface of the two phases. They are essentially balanced molecules with a hydrophilic or water-loving part, and a *hydrophobic* or water repellent portion, such as a long-chain hydrocarbon. A typical soap for this purpose consists of a sodium ion, Na^+, together with the carboxyl group COO^-, whilst the hydrophobic 'tail' is C_nH_{2n+1}, typically where $n = 15-20$, preferably 18. Another type of emulsifier or stabilizer is a water–soluble colloid, including high molecular weight water–soluble compounds such as natural gums, e.g. gum arabic (gum acacia), a naturally occurring carbohydrate, natural proteins such as casein (which is solubilised by alkali) or synthetic or semi-synthetic polymers such as polyvinyl alcohol and hydroxyethyl cellulose respectively. Natural latex is stabilised by phospholipids, also known as phosphatides, and also by proteins. Phospholipids are components of all animal and vegetable cells: they are triglycerides containing two long-chain fatty acid groups such as those derived from oleic or stearic acid, and a phosphoric acid residue attached to a base.

Why is an essentially solid material, such as natural latex considered as an emulsion, which is a fine dispersion of one liquid in another in which it is insoluble? This is connected to the manufacture of polymer emulsions by the process of emulsion polymerisation (see Chapter 3). The simplest process consists of forming a stable emulsion of one liquid (a monomer) in water, and subjecting this monomer to a polymerisation process, maintaining the stability of the emulsion throughout until all of the monomer is converted to polymer. In a modification described later, the monomers may be added gradually to the polymerising emulsion.

The final product has all the characteristics of an emulsion, but, on drying, produces a film, or possibly a powder, of a polymer, depending on drying conditions (see Chapter 1, Section 4.3). It differs from a stable dispersion of a solid, such as a pigment, in that a good dispersion of the latter consists of the 'ultimate' particles of an agglomerate, which is broken down on forming the dispersion. Polymers in emulsions, being in general non-crystalline, may be subject to quite extensive further change whilst maintaining the emulsion (latex) state, e.g. they may be directly plasticised.

This illustrates the connection between the various synthetic latices (polymer emulsions) and natural rubber latex. Physically, they represent the same type of product. Chemically, all these latices are prepared by substantially the same route, although there are major technological variation and developments (see Chapter 3). Polymerisation occurs substantially by addition polymerisation of a vinyl monomer, $CH_2:CHR$, the simplest of which is ethylene, $CH_2:CH_2$. Polymers formed by emulsion polymerisation have, in general, plastic or elastic properties. A polymer is described as having elastic properties when a strip, extended to double its length, regains its original shape and length, after the applied force which has caused it to stretch has been removed. Polymers with this property are arbitrarily defined as rubbers. In most synthetic rubbers, as formed by emulsion polymerisation, all, or a large part, of the polymer molecule consists of diene units, e.g. the polymer is formed from a monomer containing two double bonds, but it substantially retains one such double bond in each unit after polymerisation. This tends, for steric reasons, to give the polymer molecule the helical chain shape characteristic of the rubber molecule.

The properties of the main classes of synthetic polymers, as described in Chapters 2 and 3, vary widely, from rigid glasses to extremely soft and sticky products, varying to some extent on the molecular weight of the polymer. Many polymers in the intermediate range also some show some degree of elasticity.

The terms copolymer and copolymerisation imply that several monomers have been polymerised together, and are usually used when it is wished to emphasise that several monomers have been included, but is often restricted to the use of two monomers. Terpolymer is occasionally used when three monomers have been copolymerised together. Polymer is used as a general term, to describe the final product, and does not necessarily imply that only one monomer is present.

3 A GENERAL SURVEY OF POLYMER LATEX APPLICATIONS

Many polymers are used either directly, as in injection moulding, or in calendering processes such as the manufacture of polyvinyl chloride sheeting. Alternatively, they may be applied in liquid form from either solution or from emulsion. In a special case, prepolymers can be polymerised, often by crosslinking (see Chapter 6) from a liquid or fusible state to a solid infusible form.

Solvents have a number of disadvantages. They are costly, and only in rare cases will a solvent recovery plant justify its original outlay. Solvents are either flammable in which case special fire precautions must be taken (e.g. in industrial establishments where large scale spraying operations take place, as in coating automobile bodies), or toxic when non-flammable chlorinated hydrocarbons are substituted, again making special precautions necessary. The use of

polymers based on aqueous media therefore has obvious advantages. Water, the cheapest possible solvent, presents no special fire or toxicity hazard, although it has the disadvantage of a high latent heat of evaporation (538 cal/g^{-1}) and a comparatively high bp ($100°$), compared with that of ethanol ($78°$) or acetone ($56°$), both of which have much lower latent heats of evaporation. The evaporation of water is also comparatively slow, because of the relative humidity of the atmosphere.

The evaporation of a thin film of many latices–almost any thickness from ~50 μ–1 mm–produces a continuous film of polymer (but see 'Conditions for film formation' in Chapter 4). As an example, an ethyl acrylate copolymer latex will deposit a continuous elastic and rather tacky film. On the other hand, latices based on vinyl acetate or butyl methacrylate form slightly brittle, continuous films if the water is removed by evaporation at ~$25°$. These latices, however, if allowed to evaporate near $0°$, produce weak, somewhat 'crazed' films of little coherence. These properties may be considerably modified with differing molecular weight of the polymers.

Various methods of modifying polymers to produce compositions with specific properties are employed. The addition of a non-volatile liquid, known as a plasticiser, has the effect of softening or flexibilising the polymers. This process of plasticisation suggests that there is a solubility of the plasticiser in the polymer, known as the compatibility of the polymer with the plasticiser.

Polymer latices may be pigmented. The pigments are wetted out or dispersed in water with suitable additives, and the resulting mixtures used as paints and coatings. Typically, a methyl methacrylate polymer latex may be used as a surface coating on polyvinyl chloride sheet to avoid a slight after-tack.

However, nearly every useful application of latex polymers is based on either a coating application (including adhesives—see Chapter 8), or as a general binding and filling agent, typically in paper coating or in non-woven fabric manufacture (see Volume 3). Many latices may be precipitated by treatment with acid or alkali, salts of polyvalent metals, or by tannic acid. For some purposes, especially in paper manufacture, controlled precipitation of the latex takes place. Similar controlled precipitation is employed with some textile processes in which positively-charged latices are exhausted on to a fabric. In certain conditions, especially with coatings based on vinyl chloride copolymer latices, the dried films are heat treated so that the polymer particles fuse together satisfactorily, imparting the characteristic tough properties of the polymer to the film.

In some latices, a polymerisable acid may be copolymerised with a monomer e.g. crotonic acid, CH_3. CH: CH. COOH, with vinyl acetate or methacrylic acid, CH_2 : CH(CH_3).COOH, with acrylic esters. The resulting latices can form aqueous solutions when made alkaline with a strong alkali, such as sodium hydroxide, or, more usually, with a volatile base such as ammonia or an amine. The alkali causes the carboxylic groups to ionise. There is usually a considerable increase in viscosity with a latex of this type on solubilisation,

since it is sensitive to changes in the molecular weight of the polymer and, sometimes, to small variations in pH. These solutions are used in strippable coatings, and are sometimes added to paint formulations to improve brushability or final gloss. In some cases, where there is no risk of alkaline attack, or application is only for a short time, e.g. in polishes, the ammonium, or amine salts of such copolymers may be used as a major component of the formulation (see Chapter 16). Because of their high viscosity, these products can seldom be obtained in the alkaline state at more than ~25% concentration. Acidification results in complete precipitation of the product –the initial emulsion state cannot be restored.

The use of crosslinking reactions is of increasing importance in polymer latex technology (see Chapter 5) where this is treated more fully.

3.1 The principal applications of polymer latices

Since adhesive behaviour governs almost all other applications, the first chapter on applications (Chapter 8) is devoted to this subject. Adhesive applications are discussed in relation to the specific substrates involved including wood and other cellular materials, paper and packaging, and a variety of miscellaneous substrates, including adhesives suitable for bonding different polymers, in relation to the methods of assembly and the performance required.

Polymer latices are widely employed in surface coatings (paints), both decorative ('architectural') and industrial. Surface coatings comprise the major industrial outlet: their use is described in detail in Volume 2.

Volume 3 describes the principles and practice of the use of polymer latex-based systems in many other industries, including building and construction products, in cement-based products and additives, sealants, flooring compositions, decorative finishes and redispersible powders, paper impregnation and coating, including beater addition, wallpaper coatings, and many speciality coatings for pressure sensitive papers, release papers, electroconductive, photographic and security papers. Discussion of the use of speciality acrylic and non-vinyl latices in leather finishing is followed by a chapter on textile applications including warp sizing, fabric coating impregnation and lamination. Finishing for specific objectives such as flame- and water-proofing, use in upholstery applications (including tufted carpets and automobile interiors), polishes, leather finishing and many other specialised applications is also discussed. Other applications mentioned include the use of latices in vibration damping systems, and in electrographic toner manufacture and other imaging applications. Use of polymer latices in polishes is described in Chapter 16, whilst the final chapter considers use of speciality polymer latices as a binder (including pyrotechnics, inks and graphic arts materials, horticultural and ground stabilising applications), in foods, glass fibre treatments, photographic and copying systems. Barrier and antistatic coatings, gravure and offset coatings and many other miscellaneous applications are also discussed.

Surface coatings and adhesives probably provide the largest industrial outlets for synthetic latices, in terms of tonnage, but these remarkable materials have many other uses as indicated in this summary.

REFERENCES

1. Blackley, D.C., *Polymer Latices: Science and Technology.* 2nd Edition, Vol. 2, pp. 118–131, 1997: Chapman & Hall, London

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