25

NEW TRENDS BASED ON PATENT LITERATURE

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Changes in production methods and the increased emphasis on environmental protection have produced continuous changes in solvent use and in the technology of solvent processing. The aim of this chapter is to analyze existing patent literature to illustrate the trends in

- the development of new solvents
- the use of solvents in various branches of industry
- the new methods of solvent processing with emphasis on solvent recycling.

25.1 NEW SOLVENTS

The developments and introduction of new solvents are discussed in Chapter 21 (supercritical fluids and ionic liquids) and Chapter 3 (terpenes). These three generic groups of materials are emerging technologies studied to address environmental concerns.

Cleaning solvents are used in many industrial applications. These solvents have typically been highly volatile, toxic, and flammable. Dichloromethane, methyl ethyl ketone, toluene, xylene are frequently used for cleaning. They have all negative features contributing to potential hazards such as high volatility, flammability, and toxicity, and they influence the natural balance of the environment. If they are to be replaced, their replacements must have equal performance – a difficult task considering their excellent cleaning properties. Two recent patents[1,2] suggest alternative solutions. 1-methyl-2-pyrrolidone is a suitable substitute for dichloromethane and methyl ethyl ketone in terms of its solvent abilities. It is less flammable and less volatile but its high cost prohibits its use in many applications. When it is blended with an alicyclic carbonate, a polar solvent, and terpene, a non-polar component, cost reaches an acceptable level and the blend can be used for cleaning paint equipment, reclamation of silkscreens, cleaning offset print rollers, printing surfaces, and as a general purpose cleaner.[1,2]

The removal of soiling and graffiti from exterior coatings requires the use of substantial quantities of solvents. Paint removers such as dichloromethane, benzene or toluene all of which which are hazardous solvents are commonly used. Several applications are needed before complete removal is achieved. Anti-graffiti coatings which are based on wax-containing compositions help to reduce solvent use. Such coating does not contain a high concentration of solvent and can be cleaned using water heated to temperatures from 120 to 190°C under elevated pressure. This cleans the graffiti but because the cleaning temperature must be higher than the melting temperature of wax, the coating is also removed and must be re-coated. An alternative method is based on the use of environmentally friendly 1-methyl-2-pyrrolidone which cleans graffiti without removing protective coating.[3]

Terpene, d-limonene, was selected for cleaning oil spills and waste petroleum products (e.g., tar or grease).[4] The combination of 1-methyl-2-pyrrolidone with d-limonene makes a good paint stripper.[5] It eliminates dichloromethane and other undesirable solvents.

Replacement of fluorine-containing solvents is yet another goal of recent inventions. A non-toxic solvent was developed for cleaning electrical parts and motors.[6] Such solvents must have high dielectric properties to prevent damage to equipment, electrocution, and/or fire. Chlorinated and fluorinated solvents which met these perfomance requirements can be replaced by a formulation according to the invention[6] which uses a mixture of aliphatic hydrocarbons and adipate, salicylate, and succinate esters. A similar composition is also proposed[7] as the solvents in the production of PVC foams.

Medical implants must have roughened surfaces or a porous coating to promote bone and tissue integration. During the manufacture of such implants, loosely adhering coating particulates and debris collect on the surface and must be removed. The conventional cleaning method involves surface blasting with particles of hard material such as alumina, glass beads, etc. This may produce cross-contamination which will adversely affect implant performance. Other methods include polishing with ice particles, dry ice particles, and chemical cleaning. An invention[8] which includes blasting of the surface with soluble solids (e.g., water soluble inorganic salts) which are then removed in ultrasonic water bath offers reduced contamination and eliminates the use of organic solvents.

A few general examples show that solvents can be optimized for better performance by mixing. Substantial amounts of solvents can be eliminated by the careful tailoring of the process and properties to the application. Post cleaning with solvent based materials can be minimized or eliminated.

25.2 ADHESIVES

When the impact of a particular adhesive technology is being assessed, all relevant factors must be considered. These include the method of adhesive production, solvents present in the adhesive itself and the cleaners and primers required for application. The current patent literature provides many examples which reduce pollution without compromising the quality of the joint. Regulations are primary drivers for this new technology with California regulations having the greatest impact. These regulations include the VOC limits imposed by the South Coast Air Quality Management District which reduced VOC limits from actual 750 to 850 g/l for some solvent contact adhesives to below 250 g/l. These limits depend on the technology and on the adhesive type.

A patent[9] provides a means to eliminate solvent from the production process of a pressure sensitive adhesive. The typical method of producing pressure sensitive adhesive involves mastication of the elastomer, dissolving the elastomer and additives in a hydrocarbon solvent, coating the solution onto a backing, and drying to remove solvent. The phenolic tackifying resin of the invention eliminates the use of solvent process.

But often solvents must be used in adhesives in order to lower their viscosity so that product can be applied without the use of extensive force and so that the adhesive can flow into small openings in the substrate surface to promote mechanical adhesion by anchoring. The easiest formulating technique is to add solvent. This is simple and there is no need to develop new polymeric material. This is particularly true of polyurethane based adhesives which require either a special blending techniques or manufacture of the polymer with low viscosity polyols to reduce its viscosity. However, formulation of polyurethanes without solvents is technically possible as shown in patents for an automotive adhesive[10] and a general purpose adhesive.[11] In these areas additional research will bring dividends but the current effort lags behind the needs.

In some adhesives, the total elimination of solvents is not possible. The best example is that of a solvent contact adhesive which is composed of solvent and a rheological additive. The solvent performs the essential function of swelling the adjacent surfaces of the polymeric material surfaces which are to be bonded. Until recently it seemed that coping with California regulations with such adhesives systems would not be possible. However, a recent patent[12] shows that not only can the amount of volatile solvent be reduced to fulfil California requirements but also the toxicity of the solvent can be reduced and its flash point increased without compromising the performance characteristics of the adhesive. In earlier concepts of contact adhesives very volatile solvents, such as tetrahydrofuran and methyl ethyl ketone were the ones most frequently used and this was based on the premiss that such solvents would penetrate the polymer rapidly and be removed from the material immediately after swelling occurred. This type of adhesive is particularly well suited when used in plastic piping systems where the assembled system must be tested before it is enclosed in partitions. This approach eliminated the use of very volatile solvents which evaporated to become air pollutants and, to provide adequate open time, were used in excess which generally led to dripping from the joint and consequent waste of adhesive. In the invention, 1-methyl-2-pyrrolidone is used in combination with dimethyl adipate and some aromatic hydrocarbon to produce an adhesive known for its ease of use, long term durability, application with no special equipment, low cost, fast cure, and low concentration of total solvent.

In other invention[13] concentration of solvent in a fumigation adhesive used for bonding polyethylene to polyethylene in agricultural applications was also reduced by the reformulation of the copolymer used in the adhesive.

For cleaning/priming operations there are also new developments. One trend is to apply the primer in a water based form.[14] In this invention, a water based primer was developed using water reducible polyurethanes. The primer is for general use but has been optimized for use with construction sealants where solvent based primers are most commonly used today. Another approach is to use environment friendly solvents such as terpenes for both cleaning and priming. But some attempts are misguided. In one case, it was proposed to replace the primer with an isocyanate, which does not evaporate readily therefore fulfils a requirement of the regulation, but exposes applicators to extremely toxic material. Attempts of this kind must be discouraged because regulations are not designed to cope with such a gross misuse of knowledge of chemistry.

One invention[15] consists of a multipurpose cleaner/primer for roofing membranes. These elastomeric sheets are normally powdered with talc to prevent interlayer sticking in the roll. Instead of using separate cleaning solvent followed by a primer application the product of invention was able to bond the talc and other contaminants to the membrane and provide a tacky surface to promote bonding to the roof substrate.

These examples show that there are many opportunities to reduce or eliminate solvents from adhesives. These usually require a more intensive R&D effort but lead to safer and higher performance products.

25.3 AEROSPACE

Information on inventions related to solvents used in the aerospace industry is sparse (13 patents in last 25 years compared with 935 for adhesives in the same period). The reason is the secretive nature of the industry with respect to new technology and the reliance on proprietary technology to maintain a technological advantage. There is certainly a move towards limiting the solvent use in aerospace industry as discussed in Chapter 14 but the primary objective is always the performance of the applied technology.

Aerospace materials must have high solvent resistance.[16-20] Patents[16-20] which demonstrate this also stress the need for high quality and uniformity in the materials used. For these reasons, solvents were used to extract low molecular weight components which could be detrimental in space where materials vaporize or degrade extremely rapidly. Also, solvent removal after processing is emphasized to eliminate odor and remove components which may cause degradation of material exposed to highly a degrading environment.

25.4 AGRICULTURE

Recent patents describe the use of solvents to improve the properties of agricultural chemicals. In one invention, a carrier was developed from an agglomerated composition of plant fibers and mineral filler. The purpose of the carrier is to absorb and hold a large quantity of pesticide until it is delivered to the application site. The pesticide must be in a form of low melting liquid. In order to reduce its melting point, solvents selected from aromatic hydrocarbons are used to dissolve pesticide.[21] In a water dispersible composition of insecticide, solvent is used to convert insecticide to a liquid form at room temperature.[22] Solvents proposed for this application are from a group of alkyl aromatic hydrocarbons, methyl esters of alkanoic acids, and ester mixtures derived from plant oils.

25.5 ASPHALT

In various asphalt processing methods, the rheological properties of the compounded asphalt are of primary importance. One invention[23] shows how, by blending different fractions of crude oil, the processing properties can be optimized for pavement applications. In another recent invention,[24] solvent-free polyurethane was compounded with asphalt. Such products have always contained substantial amounts of solvents to reduce viscosity to the level that allows the material to be cold applied with simple techniques. Using organoclay as compatibilizer for polyurethane and asphalt and a suitable plasticizer, elimination of solvent becomes possible. In addition to environmental safety, these products can be used safely on substrates which would otherwise be affected by solvents the formulation (e.g., polystyrene insulation boards). This is one example which shows that the benefits of solvent free systems go beyond the elimination of air pollutants.

25.6 AUTOMOTIVE APPLICATIONS

Cleaning products contain the majority of solvents used in automotive maintenance. New equipment has been designed for solvent recycling.[25,26] In one such design, solvent is dispensed from a holding reservoir to a wash basin. After the parts are washed, the spent solvent is directed to a distillation chamber and condensate is returned to the holding reservoir.[25] The equipment is designed in such a way as to prevent vapor from escaping to the atmosphere. In another development a biodegradable aqueous solution of detergent is used for cleaning.[26] The cleaning solution is periodically filtered to remove solid contamination then returned for reuse. Cleaning operations are conducted under elevated temperature to increase cleaning efficiency.

In automotive refinishing shops, various cleaning liquids are used most of which are based on organic solvents. In addition to the potential of pollution, such cleaning liquids are not suitable for removal of the water soluble dirt frequently found on car body parts (e.g., tree sap, bird droppings, etc.). A cleaning composition has been designed which can clean both solvent soluble and water soluble dirt.[27] It is composed of a water emulsion of hydrocarbon solvent, an alkyl ester, and a blend of surfactants.

Extensive efforts are known to be in progress which may lead to a reduction and even the elimination of solvents used in automotive painting operations. Each coating layer is applied by a different process which may be either a water based coating or a powder coating. An example of a water based coating for an automotive base coat can be found in a recent patent.[28] The resin is derived from propoxylated allyl alcohol containing both hydroxyl and carboxyl groups and can be cured by a variety of crosslinkers. This technology is also applicable to industrial appliance coatings and wood finishes.

25.7 COIL COATING

Coil coating is performed in an enclosed system. Generally less emphasis is placed on the elimination of solvents and more to the quality of the coating. There are technological barriers to the reduction of solvent use due to the stringent rheological requirements of the coatings.

A primer layer is applied after the metal surface has been cleaned and baked. Primer plays an important role in preventing metal corrosion, therefore several performance requirements must be met. The primer layer must have good flexibility to prevent mechanical fractures and loss of adhesion of the top coats. It must not have imperfections such as blisters, craters, pops, and voids any of those will conduct water to metal surface. The transport of water to the interface depends on the properties of the primer layer and its thickness. It is preferable that primer layers are thick and can be applied in one operation. This can be fulfilled if the primer is formulated to release solvent quickly during curing. After curing, the open structure of the film should harden to a uniform, non-permeable layer. In summary, the primer should form a flexible, uniform, and thick layer. This has been achieved by the application of a hydroxy-terminated polybutadiene component formulated with a large number of solvents from the group of petroleum distillates, ethers, ketones, and alcohols.[29] The permeability of the resin has a prevailing influence on primer properties.

There are on-going efforts to reduce the VOC content of coil coatings. High-solids coatings typically contain 50-70% solid resin. Coatings higher than 70 wt% solids are more difficult to design. The coatings termed “extra high solids” contain less than 20 wt% solvent. These extra high solids coatings were made possible by the design of the resin and the selection of solvents which, in combination, give low viscosity, good flow, and a rapid evaporation rate.[30] Solvents useful in this invention are xylenes, cyclohexanone, methyl ethyl ketone, 2-butoxyethanol, ethyl-3-ethoxypropionate, toluene, and n-butanol.

Like primers, top coatings have followed a similar development path. The goal is to obtain a thick coating in one pass. Several polymers are used for coil coatings, such as polyesters, polyester-polyurethane, PVC plastisols and organosols, polyvinylidene fluoride, silicone modified polyesters, epoxy resins, and acrylic resins. A typical film thickness with all resin systems except PVC plastisols is up to about 30 μm. PVC plastisol coatings are applied to give a film thickness in the range of 80-200 μm. Because of disposal issues, chlorinated polymers such as PVC are less desirable today and have been replaced by solvent based systems. It is possible to use hot melt coatings but the high cost of equipment limits their use. In one recent invention[31] a halogen-free, heat curing coating composition was developed based on a polyester solution. The solvent combination was such that one solvent would have a boiling point of at least 160°C and preferably 220°C to allow for curing process to be fast without causing a non-uniform film. High boiling solvents can be selected from the group of aromatic hydrocarbons, esters, glycol esters, and alcohols. The concentration of solvents in this coating depends on formulation. In pigmented formulations, solvents constitute 25-40 wt% whereas in unpigmented formulations 30-45 wt%.

Liquid, single component stoving enamels were developed based on polyurethanes in which polyisocyanate component was partially or completely blocked.[32] Solvents constituted 30-60 wt% and should be mixtures of two or more components. In still another development, a retroreflective coating composition was developed.[33] It is designed to reflect the incident light beam in the direction of light source. The major application is in road signs and automobile licence plates. These had not been previously produced by coil coating. In addition to the binder components the product contains more than 50 wt% reflective glass microspheres. The solvent content is over 30 wt% of the entire composition. Another invention deals with the role of a crosslinker.[34] The crosslinking mechanism plays an important role in the performance of coating. If the crosslinker acts too rapidly, it prevents the formation of an uniform film. But if the crosslinker acts too slowly the coater must be slowed to an inefficient rate (typically belt speeds are about 200 m/min).

25.8 COMPOSITES AND LAMINATES

The performance of composites and laminates depends heavily on interfacial adhesion between fibrous component and the binding layer. Traditional technologies combine layers of prefabricated textile or fibrous component which are adhered by layers of polymeric matrix. The most recent trend involves preparation of composites on a molecular level which increases the contact surface area between both components and thus performance of the fabricated materials. One such process makes a glass/polymer composites by mixing glass and polymer on molecular level. It employs a compatible solvent to disperse materials on molecular level. The preparation of the molecular phase composite involves four steps. The first is a selection of compatible solvents and solutes. The second involves mixing a solution of glass with polymer to form a homogeneous mixture at the molecular level. The third involves removing solvent while retaining a homogeneous molecular mixture. The fourth involves forming bonds between the glass and polymer. Polar solvents are used in this application with preference given to water. Consequently, polymers used are water soluble.

The traditional polymer/glass composites (and other combinations of fibrous material with polymer) are made either by dispersion of glass fibers in the polymer carrier matrix or by intercalation of the polymer phase through a glass carrier matrix. In these processes, it is important to limit the formation of air pockets and to increase adhesion because both affect the performance of composites. For this reason, the rheological properties of the polymer matrix must be carefully controlled through the use of appropriate solvents. In composites produced from cores, the strength of the bond between facing and core must be maximized. Improved bonding has been achieved by wetting the core with solvent. The solvent serves both as a wetting agent and the adhesive solvent.[36] Due to this wetting, compressive and shear modulus have been improved by a factor of 1.4. Depending on the adhesive and the core properties, an appropriate solvent was selected from a group including water, acetone, petroleum ether, xylene, methyl ethyl ketone, methyl isobutyl ketone, and some other solvents. In another invention,[37] a decorative laminate was produced from a fabric coated on both sides with PETG copolyester. The coating contains very little volatiles.[37]

It was found[38] that a selection of solvent has effect on film thickness which is related to the boiling point of solvent. Fast evaporating solvents such as n-butyl acetate and o-xylene gave thicker coatings. Thinner films were obtained when mesitylene or diglyme were used.

A solvent-free adhesive was used for laminating vinyl sheet to wood.[39] A new technology of recycling waste carpets and textiles was developed based on coating individual yarn fibers by an adhesive containing solvent.[40] The high surface contact area produced materials with excellent mechanical properties.

25.9 COSMETICS

Two groups of solvents are used in cosmetics industry. These are process solvents which are removed after the material is prepared and solvents which are retained in product. Preparing polyaminoacid particles for encapsulation of cosmetics requires a process solvent.[41] This particular process has several stages. First, an emulsion of aminoacids is prepared which is then polymerized and the organic solvent is removed. Hollow particles can be obtained by adding a poor solvent. Such solvents belong to one of the following groups: halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons, esters, ethers, hydrocarbons. The preferred solvents are dichloromethane, chlorobenzene, and o-chlorobenzene.

Microsphere reservoirs for controlled release applications in medicine, cosmetics and fragrances are obtained evaporating solvent from an oil-in-water emulsion. The microcapsules have diameters of from 3 to 300 μm.[42] Many polymers are suitable for use in this invention which is based on the knowledge that the inclusion of plasticizer renders porous and spongy structure as opposed to the hollow core and relatively solid surface which results when no plasticizers are used.

Even smaller, nanometer size particles, can be prepared from cyclodextrin. These particles are useful as a carrier for pharmaceuticals and cosmetics. First, a solution of cyclodextrin in an organic solvent mixture is prepared, followed by the preparation of a water dispersion of surfactant. When the two components are mixed together a colloidal dispersion of microspheres is produced.[43] Particles sizes range from 90 to 900 nm. Typical solvents are methanol, ethanol, isopropanol, and acetone. Solvents are used in the purification of xanthan gum to lower ash and to obtain a product with no traces of solvents.[44] Lower alcohol is used as the solvent. Solvents have also been used to decolor fatty acid esters.[45] Crude oils extracted by pressing or with solvents cannot be used in cosmetic products. Refining processes include “chromatographic” decolorization which involves diluting the oil in an apolar solvent and absorbing impurities by contacting the resulting solution with a solid absorbent in a column. Food quality n-hexane is used as a solvent.

In some cases, solvents do remain in the final product. One such example occurs in the preparation of liquid vanillin composition used in food and cosmetics production.[46] The preparation of such a solution is complex. The solution must be pourable at room temperature, have high solids concentration (50-70%), be mechanically and chemically stable, be easy to dilute, be transparent, be stable to bacteria, and inexpensive. The solvents include water, ethanol, and propylene glycol. Polymeric liquid crystals are prepared by dispersing polysaccharide in water.[47] These liquid crystals are used for perfumes. Xanthan gum is also in use for thickening cosmetics.[48]

25.10 CLEANING

In this broad range of applications, recent work on household and electronic cleaners and metal degreasers have produced the most patents. Several patents have been selected to show progress in household cleaners. Soap scum removal and hard water deposit removal is done using a multi-component mixture containing hydrophobic cleaning solvents from the following group: dipropylene glycol mono-butyl ether, tripropylene glycol monobutyl ether, and ethylene glycol monohexyl ether.[49] In addition to the solvent, surfactants, polycarboxylic acids, hydrogen peroxide, a thickener, and water are used. A terpene-free microemulsion composition was developed based on combination of nonionic and anionic surfactants, methyl esters of C_6 to C_{14} carboxylic acids, a co-surfactant and water.[50] This is VOC-free composition for cleaning hard surfaces such as metal, glass, ceramic, plastic, and linoleum.

An aerosol cleaning composition contains surfactant, a water-soluble or dispersible solvent and a chelating agent (potassium EDTA), a propellant, and water.[51] This composition is specifically designed for the hard surfaces found in a bathroom. The composition forms foam which collapses on the stained surface to deliver the cleaning agent. The novelty is in the use of the chelating agent which enhances soil and scum removal.

A furniture cleaning and polishing compound provides protection against water.[52] This is achieved by the use of a halofluoro polymer in combination with mineral oil, a hydrocarbon solvent, silicon oil, a detergent, and water.

A thickened aqueous cleaning compound was developed for cleaning hard surfaces, disinfection, and drain cleaning.[53] The thickened product increases the residence time and cleaning effectiveness especially on non-horizontal surfaces. A firearm cleaning agent has been designed to remove the fouling residue which contains carbon and metal residue.[54] This is achieved by a combination of butyl or amyl lactate which dissolves the carbon residue and detaches the metal residue, and an electrical neutralizing agent, namely a citrus distillate, which bonds with the positive ions of the metal residue.

There are other examples of efforts to eliminate or reduce solvents but the general trend is towards optimization of formulations to perform well in a specialized application.

A cleaning liquid for semiconductor devices comprises 1-5% R_4NF (where R is a hydrogen atom or an alkyl group), 72-75% solvent, and water.[55] Solvents used in this application must be water soluble. Suitable solvents are dimethylformamide, dimethylacetamide, 1-methyl-2-pyrrolidone, and dimethylsulfoxide. Resist residues, which are formed during dry etching by the reaction of the photoresist with a reactive gas containing chlorine, must be removed because they may cause disconnections or abnormal wiring. In past, alkaline cleaning liquids were used which do not perform well under severe etching conditions.

A flux-removing cleaning composition is a water-based composition containing an alkaline salt component and a surfactant.[56,57] This formulation is designed to eliminate solvent based products.

A degreasing and cleaning compound for electronics has been developed based on a silicon containing cleaning agent (polyorganosiloxane), an isoparaffin (C_3-C_{15}), a surfactant, and a hydrophilic solvent (ethanol or acetone).[58] This formulation is intended to replace chlorinated solvents such as trichloroethane, trichloroethylene, tetrachloroethylene, and carbon tetrachloride which have been used up to now. In another invention,[59] a molecular level cleaning compound is proposed. It includes a specific solvent (n-propyl bromide), low boiling solvents (selected from the group containing nitromethane, 1,2-butylene oxide, 1,3-dioxolane, sec-butanol, ethanol, methanol), a saturated terpene, and a defluxing or ionic removing additive. The compound is designed for use in a vapor degreaser. It is suggested that this composition reduces the environmental impact because the solvents are non-flammable, non-corrosive, non-hazardous, and have very low ozone depletion potential. Superior cleaning capability of the compound is attributed to the strong solvent power of the mixture, bringing the material being cleaned into a contact with this fresh condensing solvent, and the solvent flashing action during its downward flow. In still another invention,[60] a degreasing and cleaning compound is based on non-polar hydrocarbons (C_9-C_{12} hydrocarbons or dehydrogenated terpenes), an organic polar component (alcohol, amine, ketone, or ester), water and a surfactant. In this method, residual solvent is removed from the hot article by contacting it with an aqueous medium or low boiling solvent which are subsequently removed by evaporation.

An aqueous, solvent-free degreaser contains a blend of polyoxyalkylene block copolymers.[61] This compound is intended for cleaning oils and greases from a variety of surfaces but specifically printed electronic circuit boards and automotive parts. The formulation is designed to compete with cleaning products which contain solvents. It is formulated with nonionic polymeric surfactant dispersed in water. In another development,[62] a water-immiscible hydrocarbon is used in the first cleaning step. This is followed by treatment with an aqueous displacement solution which contains surfactant and a pH modifier. The displacement solution displaces the hydrophobic solvent residue from the surface of the substrate and prevents its redeposition. The invention is intended to replace ozone depleting CFCs and chlorine containing solvents.

These patents indicate that, although there are attempts to replace solvents from formulation or to use more environmentally friendly solvents, the main requirement remains the performance of the cleaner and this is best served by using solvents. The major push has been to formulate high performance, specialized materials and processes which are carried out in an enclosed environment to prevent pollution. It should be underlined that in these applications quality of cleaning is critical and any compromise in cleaning effectiveness would contribute to an even higher environmental impact because it would lead to production of non-performing products which would have to be discarded.

25.11 FIBERS

Solvents are used in the production of fibers and in their modification and recovery from wastes. Production of fibers with optoelectronic properties for optoelectronic modulators requires several steps.[63] In the first step, a metal hydrate or a hydrated metal compound (based on Pb, La, Zr, Ti) is dispersed in solvent (ethanol, n-propanol, isopropanol, n-butanol, isobutanol, 2-methoxyethanol, or 2-ethoxyethanol), the resulting dispersion is then heated to polymerize the material and stretched to gel the fiber. The final fiber formation is achieved by heating the gelatinized fiber.

Fibers containing intrinsically conductive polymer are manufactured from a composition containing an organic acid salt of an intrinsically conductive polymer, a matrix polymer, and a spinning solvent.[64] Polyaniline is the intrinsically conductive polymer. Polyaniline alone cannot be processed into fiber because of its low solubility (standard wet spinning methods require a polymer concentration of 15-20%). Many polymers can be used as the matrix polymer. For this application, polyacrylonitrile was selected. A variety of solvents can be used but dimethylacetamide was found to be the most useful.

There are many reasons for surface treatment of the fibers. In one process,[65] introduction of functional groups is described. The equipment designed for this process includes a cleaning vessel, a vacuum drier, and a plasma treatment vessel. The fiber is first treated with a solvent, which is subsequently removed in the vacuum drier to remove all residual solvent. The surface is then modified by a plasma treatment. Cleaning removes dirt from the natural fibers and impurities from man-made fibers. Water, hydrocarbons, and halogenated hydrocarbons are used in an enclosed system. Surface etching and cleaning techniques which were used in the past released solvents and other materials to environment, especially because the fibers were not sufficiently dried.

Fiber glass is modified by the application of a thermosetting resin in two pass process. Thus treated, these fibers meet the dust free requirement for use in microchip substrate.[66] Epoxy resin is applied from a solution in methyl ethyl ketone. In another invention,[67] cellulose fibers are treated with an aqueous solution to prevent fibrillation. Fibrillation gives a hairy appearance and occurs due to the mechanical abrasion of fibers when they are processed in a wet and swollen state.

Polyester can be recovered from contaminated polyester waste which contains non-polyester components.[68] The waste may be polyester blended with cotton or other fibers, polyester magnetic tapes, or coated polyester films and engineering resins. The waste is dissolved in dimethylterephthalate, methyl-p-toluate or dimethylisophthalate. The contaminants are filtered from solution and polyester is recovered by crystallization or used as a feedstock in a methanolysis process which forms dimethylterephthalate and alkylene glycol.

25.12 FURNITURE AND WOOD COATINGS

A water based wood copolymer coating was developed to accentuate the color and the natural grain structure of the original substrate.[69] This enables solvent based system such as nitrocellulose lacquers to be replaced by waterborne coating. In another invention,[70] a water based composition was developed for covering scratches, blemishes and other damage on finished wood articles such as furniture, wood trim and wooden flooring. The inventors claim that the product has performance characteristics similar to solvent based systems. In still another invention,[71] a repair kit was developed using soluble colorants. This kit contains solvent based product. An aqueous dispersion of polyurethane is proposed for coating wood substrates such as wood floorings, furniture, and marine surfaces.[72] This product is intended to replace solvent based system, although the emulsion does contain 7% of a polar coalescing solvent (selected from the group of 1-methyl-2-pyrrolidone, n-butyl acetate, N,N-dimethylformamide, toluene, methoxypropanol acetate, dimethyl sulfoxide, and others). There is also solvent based system (solvent selected from a group of ketones, tertiary alcohols, ethers, esters, hydrocarbons, chlorocarbons). Process solvents are later stripped in the manufacturing process.

There is an obvious move in the wood finishing industry to replace solvent based systems with water based systems. This is a necessary development given that finishing processes are often carried out in homes or in small plants or workshops which lack adequate ventilation.

25.13 PAPER

Solvents are relevant in pulping processes and waste paper processing. Solvent based coatings and inks are applied to paper and paper must be designed to accept such materials without absorbing an excessive amount of solvent.

The traditional pulping process uses various inorganic chemicals to separate cellulose from lignin and other components. A major problem associated with this process is a difficulty in recovering or destroying these inorganic chemicals before they become major environmental pollutants. Solvents may be part of the solution to this problem. A process was developed in which wood is digested in a single-phase mixture of alcohol, water, and a water-immiscible organic solvent such as a ketone.[73] After digestion and adjustment of the proportion between water and solvents, lignin is present in the organic solvent, cellulose in the solid pulp phase, and hemicelluloses and dissolved sugars are in the aqueous phase.

Acceptance of the solvent pulping method has been slow due to difficulties in solvent recovery. However, apparatus and technology have been developed which allow recovery of almost all the solvent.[74] In another development,[75] it was found that pulp bleaching can be performed more effectively in the presence of a solvent, either methanol or ethanol. Alcohol protects cellulose during the ozone bleaching stage better than does water. Better quality cellulose is the result.

Wax paper is recycled by immersing it in solvent, preferably n-hexane.[76] The wax is dissolved in the solvent and separated from the paper. Tipping paper used to produce cigarette filters is made with special grades of calcium carbonate which reduce the wear of cutting knifes and limit absorption of solvent from ink.[77] Paper stock was developed for release paper with a reduced tendency to absorb solvent from the coating. This allows thinner coats to be applied which retain good release performance.[78]

25.14 PRINTING

A rotogravure or flexographic printing ink has been developed which reduces wear on printing equipment.[79] Solvents used in these inks include aliphatic, aromatic, and naphthenic hydrocarbons, alcohols, glycol esters, ketones, esters, and water. With water, glycol esters are used as cosolvents.

A lithographic ink has been developed based on an ester-modified carboxyl-containing copolymer dissolved in a solvent system selected from a group which includes aliphatic and aromatic hydrocarbons.[80] The invention gives better pigment dispersion and color development. A printing ink for gravure printing is based on a polyurethane oligomer dissolved in organic solvents selected from aliphatic, aromatic, and naphthenic hydrocarbons, alcohols, ethers, and esters.[81] Here, again, the driving force behind the invention was to increase color strength. A novel method of screen printing was developed to apply surface layers of materials with properties such as phosphorescence, electrical conductivity, mechanical adhesion, dielectric properties, etc.[82] The choice of binder and solvent depends on the substrate involved. A metallic appearance on plastic products can be obtained by applying an ink coating.[83] Typical solvents include aromatic hydrocarbons, cyclohexanone, butyl acetate, diacetone alcohol, an glycol ether. The concentration of solvents is in the range from 75 to 90%. The method of processing is UV curing. The choice of solvent depends on the substrate. The method was developed as an alternative to hot foil stamping which has numerous limitations. In another invention,[84] a device for cleaning screen plates was developed. The process used a solvent and cleans with increased precision.

A water based ink was developed for writing, drawing and marking using fountain and ball pens.[85] An organic solvent based ink was developed for ink jet systems.[86] The ink contains 40 to 98% solvent. Typical solvents include ethanol, isopropanol, acetone and methyl ethyl ketone. In still another development,[87] a water based ink jet composition was developed.

These patents show that solvent replacement is not a primary activity in this field. There is substantial interest in developing new technology for printing industry but it is driven mostly by a desire to improve quality and to satisfy needs of emerging printing technologies.

25.15 STONE AND CONCRETE

A limited number of inventions were patented in this very broad and important field of construction technology. A solvent based coating for a containment structure is based on chlorosulfonated polyethylene.[88] The coating is intended for applications in trenches, tank interiors, containment lining, flooring systems and joint overlays. The aim is to improve adhesion of the coating to the substrates. Solvents are selected from acetone, xylene, methyl isobutyl ketone, diacetone alcohol, and several other ketones and esters. A water reducible coating for concrete sealing was developed based on an acrylic resin.[89] The coating is intended to compete with solvent based coatings. It contains butyl carbinol as the dispersing solvent. A waterproofing coating was developed based on a solution of styrene polymer.[90] Solvents are chosen from among dichloromethane, ethylene chloride, trichloroethane, chlorobenzene, acetone, ethyl acetate, propyl acetate, butyl acetate, benzene, toluene, xylene, ethyl benzene, and cyclohexanone.

Efflorescence of masonry, brick, concrete, and mortar can be eliminated by coating with a polyvinylalcohol solution in water.[91] A solvent addition during silica glass production prevents cracking.[92] The most effective solvents are methanol, ethanol, n-propanol, isopropanol, N,N-dimethylacetamide, N,N-dimethylformamide, methoxyethanol, and tetrafurfuryl alcohol. Oily stains on stonework can be cleaned with petroleum hydrocarbons.[93]

25.16 WAX

This section includes a discussion of formulated products which contain wax. A fluorinated copolymer was used in a wax composition for car body refinishing.[94] A mixture of ethyl acetate, toluene and heptane is used as a solvent. A cleaning and polishing composition for automobiles is also based on a fluorinated polymer and contains hydrocarbon solvent at up to 70%.[95] Universal auto lotion is a water/solvent emulsion of wax.[96] It contains isoparaffinic solvents. A car polish formulation contains 10-35% mineral spirits.[97] A semiconductor polishing composition contains alcohols, acid and water.[98]

25.17 SUMMARY

The patents evaluated show that the inventions address the needs of the industry. All industries seek to improve or optimize product performance. Elimination of solvents in these inventions is secondary. This does not mean that there is a lack of awareness of environmental impact. In some industries, such as, for example, the aerospace industry, quality is so important that the best solution must be found even if it is not the least polluting. The best opportunity for solvent replacement are in industries which are known to have limited capabilities to protect employees by the use of protective equipment, such as the furniture industry. There are industries which need to be more concerned about pollution but do not seem to have developed new products with this in mind (at least by the account of existing patents). This applies to the metal stamping and processing industries, industries supplying DIY markets, asphalt processing industries, concrete coatings, etc. There is little emphasis placed on pollution by these industries because they are made up of small, frequently, one-man operations and thus they are very difficult to assess. This also brings up the issue of the investment required to improve the environmental record. For example, automotive industry was able and did invest in environmental protection and the results are clearly beneficial.

It is interesting to ask the question “will solvents eventually disappear from the industrial environment?” The above discussion shows that many new technological processes are developed based on solvents. There are more new products containing solvents than there are inventions aimed at their elimination. So, in spite of a strong desire to eliminate solvents their production volume continues to increase slightly. One might ask if this approach is legally, politically and morally acceptable given that the general public see solvent elimination as a benefit. Or are the efforts being made simply directed at finding the least harmful means of delivering the product which the public demand. Above examples show that, although sometimes solvents are introduced in new processes which previously did not use them, the overall objective of having a lower impact on the environment seems to have been met. The paper industry example shows that the use of solvents in a well designed plant can be less harmful for the environment than traditional pulping. Technologies aimed at reprocessing wastes provide more insight. A large number of studies on polymer blending have shown that reprocessing of mixed plastics, usually conducted without solvents, results in products which are not useful. In order to make recycling work effectively (especially of products which are multi-component mixtures such as composites, laminates, coated fabrics, coextruded films, etc.) some means of material separation must be found and the use of solvents offers just such a possibility. This brings several questions: which solution is better? should we dispose of these materials in the soil and wait for 50-100 years until they are digested? or should we responsibly use solvent under controlled conditions which does not pollute water, air and soil and does not endanger workers and customers? Solvent use can meet public needs and modern technology can find ways to ensure that solvent emissions are not released to the external environment.

Chapter 14 has several examples that show that many solvent releases can be avoided by elimination of negligence and sloppiness. For example the majority of solvents emissions from the petroleum industry can be avoided if valve leaks are repaired. This does not require extensive research but adoption of simple engineering principles to rectify the situation. The patents discussed above teach us that solvents can be eliminated or their amount reduced if resins are reformulated to reduce their viscosity thus eliminating the need to add solvents. In many cases where products are reformulated, this option is completely neglected due to the fact that the formulator finds it easier to use solvents since they usually do not affect other process characteristics or material performance and provide the simplest tool to adjust application properties. More knowledge must be acquired and more research is required than is currently being expended in product development. Solvents are inexpensive and this tends to encourage their use to lower the cost of the product. If situation develops that allows manufacturers to be able to profit from solvent-reduced or solvent-free formulations many products will be reformulated accordingly. But this requires that the environmentally aware customers be willing to pay premium prices for products which are solvent-free.

The other option for future improvements, which is certainly being exercised as is shown in the above patents, is a rationalization of solvent composition. Here, regulations have played a progressive role in eliminating or reducing some very harmful materials. New inventions are still needed which aim to find more benign solvent mixtures or to replace resins which require aggressive or harmful solvents by ones which allow for more environmentally friendly compositions.

There are many technological processes which will continue to require solvents at the highest levels of technological development. In these instances, good engineering practices will take the place of solvent elimination. There is nothing wrong with using solvents in a responsible manner. Scientific and engineering evaluations of all options and an assessment of the total social costs and benefits will show the best ways to optimize products and processes.

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