При використанні як полімерної складової сумішей БД спостерігається сповільнення процесу зшивки (композиції V' і VI') внаслідок пропускання променів через скло. Аналогічно ведуть себе композиції, що містять рідкий каучук "Krasol LBH-3000". Як і в випадку композиції IV', композиція VIII' на основі промислової епоксидної смоли має значно менший вміст зшитих продуктів порівняно з композицією VII'. Це ще раз підтверджує участь пероксидних груп смоли ЕД-20П у формуванні тривимірних структур.

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INDUSTRIAL APPLICATIONS OF PHOTOCURING – A SHORT OVERVIEW

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Стаття присвячена деяким аспектам використання фотоініціюючої полімеризації у різних галузях промисловості, в яких її успішно застосовують. Процес застосовується під час полімеризації жорстких мономерів, олігомерів і преполімерів, які структуруються під впливом УФ-опромінення видимого спектру (350-600 нм).

This paper deals with some aspects of application of photocuring within the different industrial sectors, where this technology has successfully been implemented. Photocuring means to harden (crosslink) monomers, oligomers and prepolymers and dry varnish or plastic with the influence of UV and/or visible (350-600 nm) radiation.

The photocuring has been known to industry for more than 20 years. The process has undergone continuos development. The extension of photocuring into new applications poses new design challenges to increase photocure efficiency and speed (reduction in process time), to develop the best physical and mechanical properties of the cured material. Nowadays, about 30,000 UV industrial photocuring lines are in operation all over the world [1].

The main components of a photocurable material are mono- and polyfunctional meth(acrylic) monomers, oligomers, prepolimerized resins, photoinitiators, pigments, extenders, inhibitors and stabilizers. Radicals can essentially be formed by two mechanisms: photofragmentation or by charge-transfer complexes in which electron/proton transfer occurs [2-7].

SUMMARY OF PHOTOCURING APPLICATIONS [8-10]

Converting, printing and finishing:

- labels: letterpress, flexo and screen printing on paper and film.
- business forms: offset printing on paper.
- magazines: offset printing and overprint varnish on paper.
- cardboard packaging: offset printing of liquid and dry food packaging.
- film: gravure and flexo printing for food and non-food packaging.
- corrugated board: flexo varnish for high gloss packaging.
- cup and tube: off-set printing and varnishing on mandfrels.
- plastic containers: silk-screen printing and varnishing on bottles.
- metal containers: basecoats, off-sett print and overprint varnish.

Coating on flexible and rigid substrates:

- silicone release on filmand paper.
- pressure sensitive adgesives.
- gravure coating on decorative papers.
- optical coating for solar films.
- fiber optical coatings.
- abrasion-resistant coatings.
- antifogging films for protective covering (from humidity, dirt, dust, and chamical contaminants in the end-use environment) over military and aerospace applications.
- weather-resistant coatings, sol coatings.
- light-reflective coatings for road signs or marks.
- photoluminescent coatings.

Electronics:

- adhesives: component fixation of electrical components.
- conformal coatings: dipor spraycoating of protective coating on printed circuitboards.
- polymer thick film: conductive inks on printed circuitboards.
- ink-jet: marking of cables and components.
- potting: connectors and components.

Optics:

- manufacture of compact discs, vide discs and laser disks.
- optical lens coatings.
- coatings for color filters
- photocurable polymers for nonlinear optics.
- holographing imaging and computer-generated holograms.
- holographic optical elements such as diffraction gratings, mirrors, lenses, wave-guides, and so on.
- Fourier filters for shape recognition operations.

Wood:

- clear coatings: primer and topcoat.
- pigmented coatings: primer and topcoat.
- fillers: clear and pigmented.
- laminates, veneers and panel boards, wooden household furniture, wooden floor tiles.

Medical:

- adhesives: bonding of medical plastic assembles.
- special coatings: medical utensiles, microporous coatings for use nonwoven products as barrier materials (for bacteria in airborne and solution-borne media) or to achive a high degree of water repellency, usable in sterile, breathable, disposable medical nonwovens (hospital end uses, medical packaging, wound dressing) or in breathable, water- or liquid-impermeable.
- dental: restorative resins [11-14].
- sterilization.
- surface activation of plastics.
- bioerodible gels.
- ophtalmic lenses, manufacture of resin lenses for protecting the eyes from UV radiation, laminates for lenses, artificial eyelens material for cataract operations, and spectale lenses.

Automotive:

- 3D plastic parts: base and top coat for metalized objects, headlamps.
- windshield: black screen printed edges on wind shields.
- adhesive: adhesives for bonding polycarbonate lense to main headlamp reflector body.

Pigmented coatings usable in the paint industry:

- photocuring of paints and lacquers as thick coatings is very difficult because of the absorption of the incident light by the pigments. This technology has been successful only when drying thin films of printing inks. Many attemps have been made to solve this problem by using alternative methods based on hybrid cure or dual cure, which requires a complicated multistep process.

PHOTORESISTS APPLICATIONS [10]

Photopolymers for lithography and graphic applications in general and photoresists for microelectronics represent the highest market share among the other applications of photocuring. During the last decade the progress of prepress technology towards electronic data handling and of submicronlitography towards increasing circuit densities imposes new trends in the design of photosensitive polymer coatings.

In the graphic arts as well as in microelectronics photosensitive coatings are characterized by their ability to reproduce image patterns on suitable substrates. Direct pattern transfer (Positive mode) and reverse pattern transfer (Negative mode) can be realized. In both modes the processes can be split up to into three major steps:

- the photochemical reaction taking place in the coatings creates a solubility differentiation between the irradiated and the non irradiated areas.
- this solubility differentiation is exploited during the development step.

- selected parts of the polymer coating are hereby eliminated, leaving a positive or a negative reproduction of the original image.

The transferred patterns can be used in a final processing step as a resist layer, temporaily preserving the substrate during etching or doping procedures in microelectronic technology.

In litographic printing on the contrary the photochemically crosslinked photopolymer pattern is used as an essential element of the printing process [15]. It accepts and transfers greasy ink in offset printing technology. The laser imaging technique allow to obtain high quality graphic arts. The prime importance of laser imaging systems is their ability to act as digital output imagers for electronic publishing. Laser typesetters and four-color electronic publishing systems are already available.

In classical negative mode working photopolymer the solubility differentiation is obtained by photochemical insolubilization of the coating either by photochemically initiated polymerization of multifunctional monomer compositions or by photochemical crosslinking of light-sensitive preformed macromolecules.

In classical positive mode working photopolymer systems the solubility differentiation is obtained by photochemical destruction of a dissolution inhibitor or by photogeneration of a dissolution promotor.

COATING OF WOODEN SURFACES

Furniture surfaces are usually treated with a protecting lacquer which should keep their wooden structure and wooden appearance. The use of UV/vis radiation curing processes in wood finishing lines: wood floors, kitchen cabinet finishes and flat board finishes are recently commercial.

THREE DIMENTIONAL SOLID IMAGING[16-23]

The solid imaging (called also: stereolitography, three-dimentional (3-D) photopolymerization) is the method of the direct production of three-dimentional models and parts from digital design information from a three-dimentional CAD (Computer Aided Design) system to guide the formation of a model that closely represents the original design. The 3-D photocuring involves computer controlled laser exposure into a vat of liquid photopolymer [18,24,25]. This technology allows to reduce the time and expense necessary to design and manufacture prototype parts for automotive and aerospace industries, as well for the medicine [26]. However, the introduction of the medical stereolitography models into the hospitals is going slower than the introduction of 3-D photopolymerization into industry.

The interest in solid imaging technology has a number of advantages:

- rapid translation of a design to a physical form.
- decreased turnaround time and cost for parts and products that require redesign.
- rapid generation of new mold and patterns.
- manufacture of parts that are difficult to prepare by conventional milling or casting techniques (e.g.hollow turbine blades).
- easy replication of three-dimentional electronic data (e.g.mathematical equations, medical imaging, topographic maps).
- development of materials that will have mechanical and physical properties approaching those of rigid and flexible engineering plastics.

- design of materials of lower toxicity tha will be suitable for an office environment.

PROBLEMS WITH PHOTOCURING IN AIR (OXYGEN)

Molecular oxygen exists in the electronic ground state as the triplet state and is a diradical. Its lacks the energy to initiate polymerizations, and, therefore, is considered stable. While not being able to initiate polymerizations, it does readily react with already existing radicals to produce peroxy radicals, which do not propagate polymerization reactions. Peroxy radicals acts as chain transfer agents via a hydrogen atom abstraction route, resulting in chain termination. In this way oxygen is very efficient polymerization inhibitor. The most obvious way to eliminate oxygen inhibition is to eliminate oxygen. The most efficient way is through the use of nitrogen blanketing. In industrial applications some draw backs of this approach include the fact that nitrogen blanketing is another cure parameter that must be controlled and monitored, and units with a nitrogen purge often cost more than units without.

Other methods of eliminating oxygen include:

- addition of small amount of paraffine wax. As polymerization begins, the wax rasies to the surface, blocking out additional oxygen.
- covering of photocured surface with thin polymer film (eg.mylar or similar plastic). This prevents of penetration of oxygen into the system.
- inreasing amount of photoinitiator used. Higher concentration of initiator will cause more energy to be absorbed which in turn will lead to more radicals being formed. This will increase the cure spead.
- increasing the amount of energy that the system is irradiated, by slowing the speed of line slighty or by increasing of the number of lamps that are used.
- addition of small amounts of tertiary amines which are better hydrogen-atom donors than an acrylated monomer. This mechanism consumes peroxy radicals, yet yields a new, reactive free radicals. However, adding of amines, tend to hurt shelf life, color, and other film properties. Some factors which influence the choice as to weather an aliphatic or aromatic amine is used include the fact that, reputedly, the aromatic amines lead to less yellowing than aliphatic amines of the photocured material and that the aromatic amines are much less hydrophyllic than the aliphatic amines. Thus, the choice as to which amine is used is often determined by the nature of the process to which the photocurable mixture will be sybject and also the end use of the cured material.

POLYMER DEGRADTION DURING THE PHOTOCURING

A major case of polymer degradation is a photochemically induced oxidation [27-29]. The polymer backbone absorbs UV energy and undergoes a chain scission. This causes free radicals to be formed on the polymer which will react with oxygen. The peroxy radical which is formed then abstracts a hydrogen-atom from the polymer, thereby, creating a hydroperoxide and another free radical. The hydroperoxide is reactive to UV radiation and will break down to form two more reactive radicals. The process continues and the cured material is eventually ruined. The use of UV absorbers or radical scavengers are often used to stabilize a photocured material agains photooxidative degradation [27,30].

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Note: Dr Julita Jakubiak is a Head of a joint project "Mechanisms, kinetics and applications of photopolymerization initiated by visible light photoinitiators". Prof. Jan F. Rabek is a scientific adviser of this project.