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Studies on degradation of poly(ethylene oxide) by multistep pyrolysis/gas chromatography with a programmable temperature vaporization injector

RAPID COMMUNICATION

Summary — The multistep pyrolysis/gas chromatography technique using a programmable temperature vaporization injector was used to study thermal and photochemical properties of polymers. Pure poly(ethylene oxide) (PEOX) and PEOX + 3% $CoCl_2$ specimens, 20-μm films, were UV-irradiated (2.45 mW/cm^2) for 2 and 4 h in air at room temperature and pyrolyzed/gas chromatographed at 200°C, 420°C and 500°C (Fig. 1, 2). The products evolved at 200°C included residual solvent, monomer, catalyst, polymerization additives, and processing aids. At 420°C, degradation attained maximum and the compound concentrations were maximum in PEOX UV-irradiated for 2 h. In the 4-irradiated PEOX, the 420°C chromatographic peaks were less intense. At 500°C, the intensity of the peaks rose as the irradiation time was prolonged. $CoCl_2$ (3%) gave rise to new degradation products. At 420°C and 500°C, irradiation had negligible effect on degradation of PEOX + 3% $CoCl_2$. Scheme 1 illustrates the major interactions accompanying thermal and photochemical degradation of PEOX in the presence of $CoCl_2$.

Key words: poly(ethylene oxide), poly(ethylene oxide) + 3% $CoCl_2$, UV-irradiation, pyrolysis/gas chromatography, programmable temperature vaporization injector.

Recently, a wide variety of sophisticated methods have been applied to study the mechanisms and kinetics of polymer degradation [1—5]. For example, thermal analysis (TGA, DTG, DTA or DSC) is a useful tool for characterization of polymer properties [6—9]. Not only thermal resistance but also photostability of polymers can be estimated by these techniques [9]. Another method useful for the detection of degradation products is gas chromatography [10—12].

Recently, a new technique, *viz.*, thermal desorption programmed/pyrolysis coupled with gas chromatography was developed to study plastics, polymers and their blends [13, 14]. The chromatogram obtained at a carefully selected temperature gives a characteristic pattern of the polymer under investigation and is called the "chromatographic fingerprint" [15—17].

The aim of this work is to investigate the effects of UV-irradiation on pyrolysis of poly(ethylene oxide) (PEOX) and of cobalt(II) chloride on photo and thermal degradation of this polymer by using the Multi-Step Thermal Desorption Pyrolysis/Gas Chromatography technique performed by using a Programmable Temperature Vaporization injector (PTV).

This work is a continuation of our previous studies on accelerated photodegradation of PEOX in the presence of $CoCl_2$, in which we followed changes caused by UV-irradiation by using FT-IR, UV-Vis spectroscopy, viscosimetry and gel permeation chromatography [18].

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEOX) from Aldrich and $CoCl_2 \cdot 6\,H_2O$ from POCh (Poland) were used in this study. Number-average molecular weight of PEOX was equal to 18 700.

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Photodegradation

Thin polymer films (20 μm) prepared by evaporation of the solvent from aqueous 2% solutions were UV-irradiated by using a low-pressure mercury vapor lamp (TUV 30 W, Philips, The Netherlands). The light intensity at the sample position, as measured by an IL 1400A Radiometer (International Light, USA), was equal to 2.45 mW/cm^2.

Instrumentation

A programmable temperature vaporization injector (OPTIC-2, ATAS, Cambridge, UK) connected with a gas chromatograph (Varian 3400, USA) was used. The chromatograph was equipped with a 20 m x 0.3 mm ULTRA 1 column (Hewlett Packard, California, USA) containing a 0.5 μm stationary phase. The GC was equipped with a flame ionization detector (FID). Helium (70 kPa) was used as a carrier gas. The instrument has been described in detail by van Lieshout *et al.* [13, 14].

Analysis

Temperature levels (200, 420 and 500°C) for thermal desorption and pyrolysis were selected on the basis of thermogravimetric curves of PEOX. The lowest temperature, 200°C, at which the sample is still stable, was used for monitoring traces of solvent, monomer and other volatile additives adsorbed on the polymer surface. The second temperature, 420°C, was chosen for the highest rate of PEOX degradation. At the third temperature, 500°C, the main step of thermal decomposition of PEOX was already completed, thus, at this temperature, the products evaporating from pyrolysis residues were monitored.

A sample, 3.5 mg, was loaded into the glass liner containing a glass frit in the middle. Then, the liner was placed in the heated zone (PTV injection). After closing the system, air was removed by passing helium gas (100 ml/min) for 90 s. The initial temperature was 37°C, the temperature of the detector was 350°C. The desorption time at each of the three temperature levels was 30 seconds, the heating rate of the PTV was 16°C/s and the heating rate of the GC was 20°C/min. The end temperature of the GC was 295°C.

The split injection method was used. The split ratio was 1:66, *i.e.*, only approximately 1.5% of volatile products formed were transferred to the GC column. The column flow was 1.5 ml/min, the split flow was 100 ml/min.

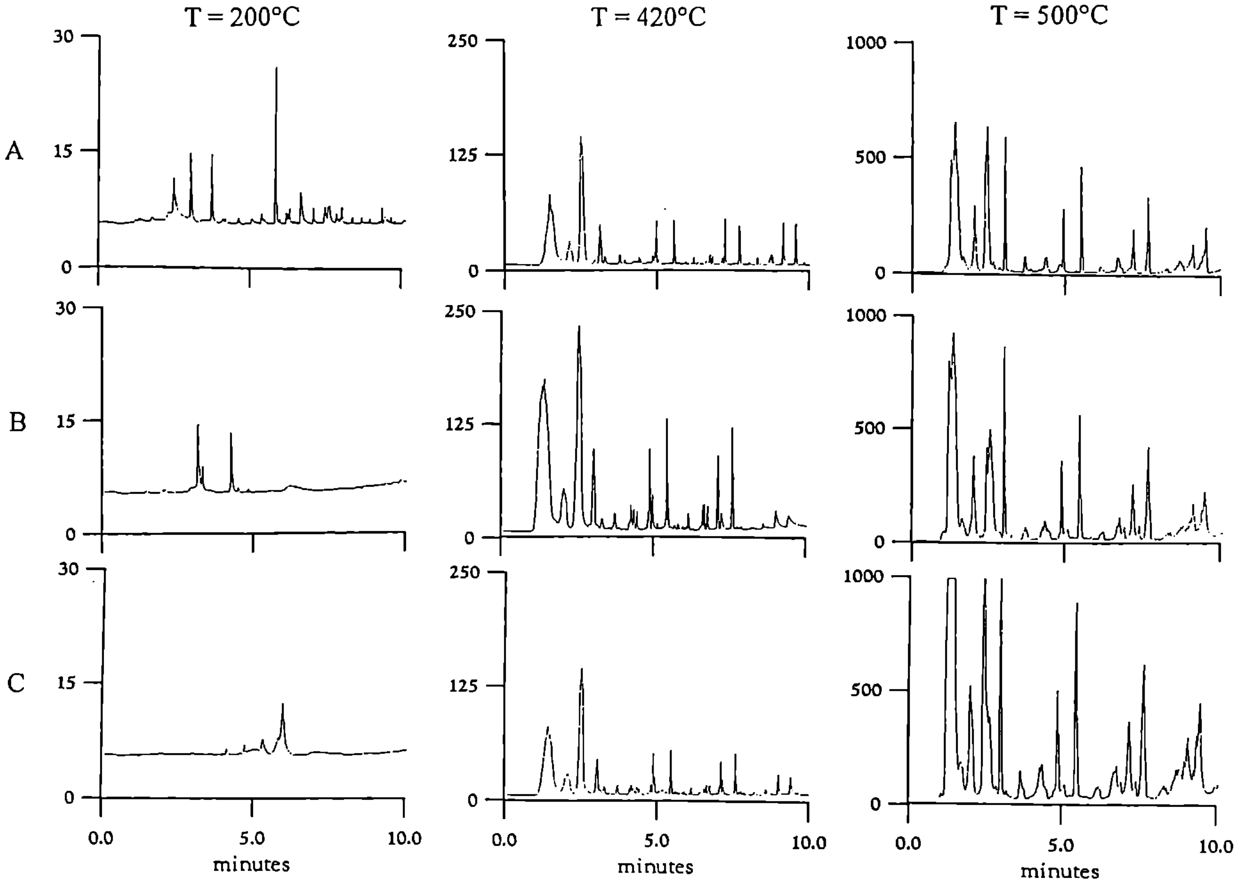


Fig. 1. Gas chromatograms of products released during pyrolysis of PEOX at 200, 420 and 500°C: A — nonirradiated polymer, B — after 2 h of UV-irradiation, C — after 4 h of UV-irradiation

It should be noted that CO_2 and H_2O are not detected by FID.

RESULTS AND DISCUSSION

On being heated, PEOX releases a large number of volatile products. The chromatograms recorded at 200, 420 and 500°C for nondegraded and UV-irradiated PEOX are shown in Fig. 1.

As compared with the 2 h or 4 h UV-irradiated PEOX (Fig. 1 B, C; 200°C), the pure unirradiated PEOX (Fig. 1 A; 200°C) is seen to release the larger number of the volatile products formed at 200°C. The amounts depend also on the past history of the sample. The UV-irradiated sample generally produce less intense peaks. This fact points out that major volatilization occurred during the exposure to UV light. The products evolved at this lowest temperature include mainly the residual solvent, monomer, catalyst and other additives added during the polymerization or processing steps.

The kind of products monitored at the maximum rate of PEOX degradation (at 420°C) is for the nondegraded samples almost the same as for the UV-irradiated samples (Fig. 1 A—C; 420°C). The highest concentration of these compounds was observed in PEOX after 2 h of UV-irradiation. This fact suggests that the photodegradation products included in the polymer matrix enhanced thermal decay of PEOX. In particular, hydroperoxides formed in PEOX during UV-irradiation are known to be thermally unstable. They decompose to form hydroxy (HO·) and alkoxy (RO·) radicals, which can reinitiate polymer degradation [5]. In the 4 h UV-irradiated PEOX, the intensity of the chromatographic peaks (after treatment at 420°C) decreased. After this period of exposure, photodegradation of PEOX is likely to have been very efficient. The compounds released during this step are mainly products of main chain scission as well as photooxidation products containing functional groups (carboxyl, hydroxyl, internal or end double bonds) formed during UV-irradiation in air. The major volatile species appearing on thermal and photochemical degradation of PEOX have been reported to be ethylene oxide, water, carbon dioxide, formaldehyde, acetaldehyde, formic acid, acetic acid, ethylene, methyl formate and ethyl formate [19—23].

Other noneasily volatile and more stable products were detected in PEOX at 500°C (Fig. 1 A—C; 500°C). Interestingly, the intensity of all these peaks increases with the irradiation time of the polymer. For example,

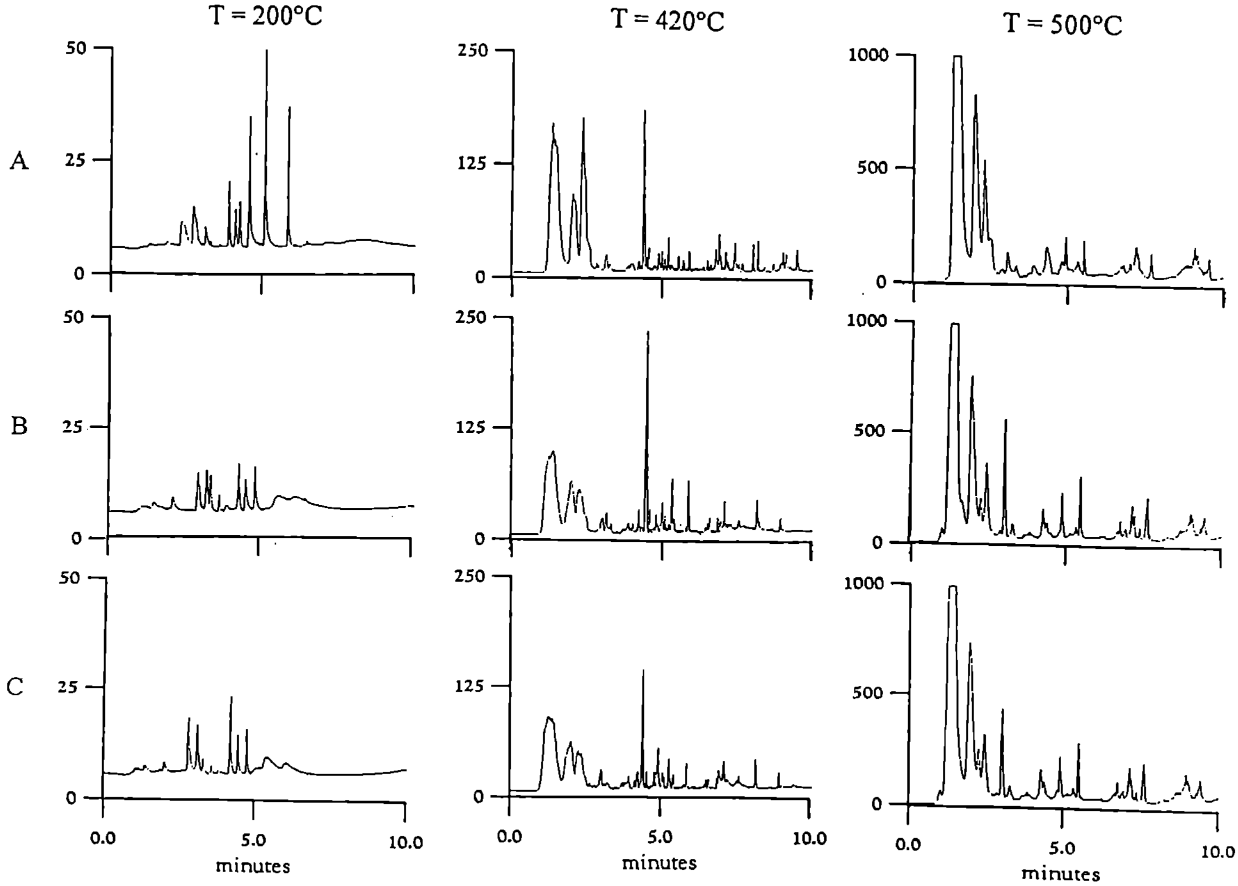


Fig. 2. Gas chromatograms of products released during pyrolysis of PEOX + 3% $CoCl_2$ at 200, 420 and 500°C: A — nonirradiated polymer, B — after 2 h of UV-irradiation, C — after 4 h of UV-irradiation

the peaks in the 4 h UV-irradiated PEOX (Fig. 1 C; 500°C) are about twice as high as those in nondegraded PEOX (Fig. 1 A; 500°C).

It should be mentioned that each PEOX sample heated up to 500°C produced about 7% of a carbonized solid residue. The different efficiencies of volatilization are thus seen to have no influence on the amount of the polymer residue. Probably, the molecular weights of the photoproducts evolved are very low, and thus weight changes in the PEOX pyrolyzates could not be detected.

$CoCl_2$ added to PEOX matrix caused formation of new degradation products (Fig. 2) compared to pure PEOX heated at the same temperature. The chromatograms recorded at 200°C for PEOX + $CoCl_2$ contained more peaks and the intensities of these peaks were higher

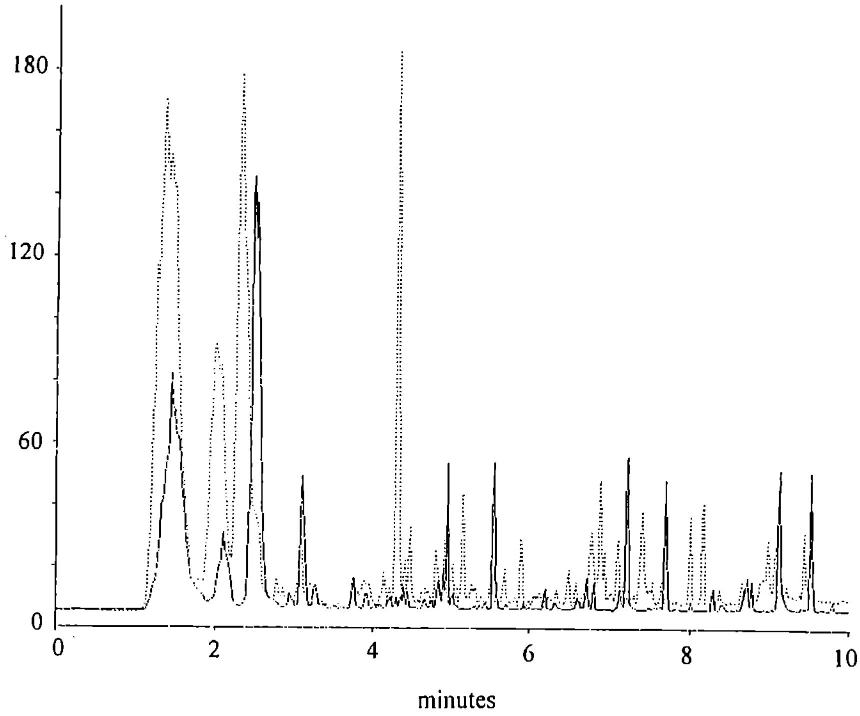


Fig. 3. Comparison of the chromatograms of nonirradiated PEOX (·····) and PEOX + 3% $CoCl_2$ (——) recorded at 420°C

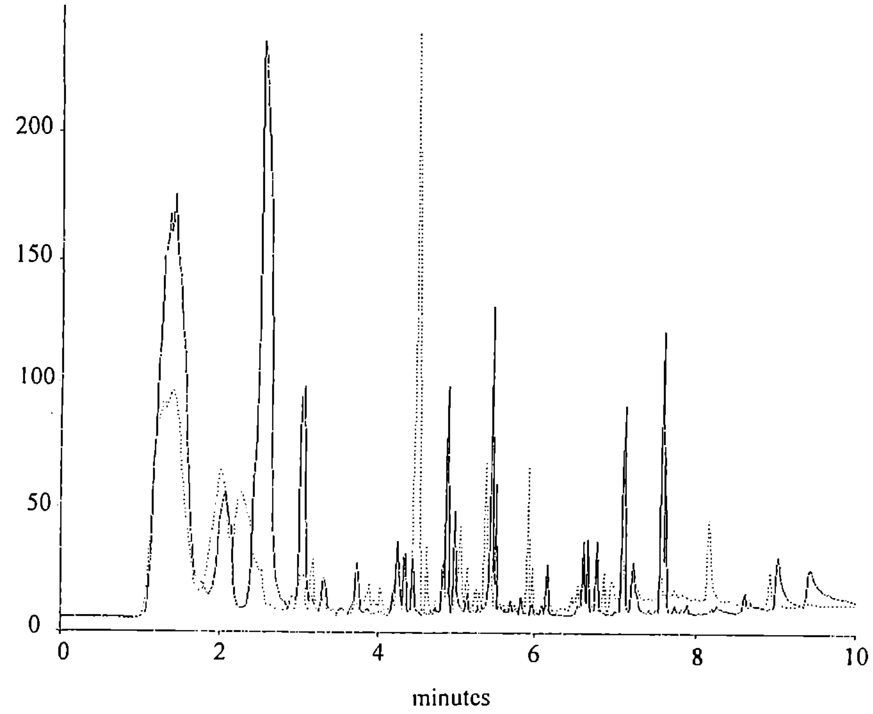


Fig. 4. Comparison of the chromatograms of PEOX (·····) and PEOX + 3% $CoCl_2$ (——) after 2 h of UV-irradiation recorded at 420°C

compared to those of the corresponding peaks in pure PEOX. Here again, the degree of volatilization was larger for the unirradiated PEOX + $CoCl_2$ sample.

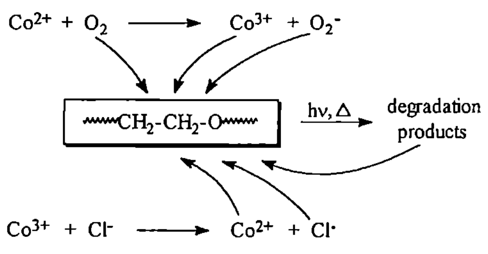
The effect of UV-irradiation in PEOX + $CoCl_2$ in the second and third step of pyrolysis (*e.g.* at 420 and 500°C) is insignificant.

For a clear presentation of the $CoCl_2$ influence on the course of PEOX degradation, examples of overlaid chromatograms are presented in Fig. 3 and 4. For instance, in the presence of the cobalt salt, a new large component appeared in ~4.5 minutes in the unirradiated samples (heated at 420°C). Moreover, the peaks monitored after the first 3 minutes were shifted to shorter retention times and, simultaneously, the intensity of these peaks was much higher in PEOX + $CoCl_2$ than that in pure PEOX (Fig. 3).

In the case of 2 h UV-irradiated samples, besides the greatest peak at 4.5 min, two following new peaks were observed in the presence of $CoCl_2$: in ~6 and 8 min (Fig. 4). Other peaks in PEOX + $CoCl_2$ were smaller than that in PEOX, which clearly indicates that some unstable degradation products were released earlier during polymer exposure to light, These products can interact with the polymer and accelerate is further decomposition.

A comparison of the chromatograms of PEOX and PEOX + $CoCl_2$ recorded at the same temperature allows to conclude that the cobalt salt accelerates thermal decomposition of PEOX. It confirms our earlier findings by other techniques [18]. Furthermore, different new degradation products formed in the presence of $CoCl_2$ indicate that the mechanism of PEOX degradation has changed. In other words, the cobalt salt changes the chromatographic fingerprint of PEOX during pyrolysis.

The enhanced degradation of PEOX in the presence of the cobalt salt is mainly caused by its catalytic action. Co(II) cations undergo reversible oxidation to Co(III) by atmospheric oxygen. Co(III) can react with PEOX as well as with Cl^- anions. In this latter reaction active chloride radical-atoms are formed. They can abstract hydrogen atoms from PEOX chains and the degradation cycle is repeated (Scheme I).



Scheme I. Main interactions during thermal and photochemical degradation of PEOX in the presence of $CoCl_2$

Summarizing, the present simple method is seen to enable polymer degradation products evolved at different temperatures to be fast detected. This is important in environmental protection because such volatile products diffuse from polymer matrix and pollute the atmosphere. Moreover, they can have harmful influence on living organisms.

CONCLUSION

Multi-Step Thermal Desorption/Pyrolysis/Gas Chromatography allows us to predict the chemical compounds which will be evolved during polymer degradation (aging), for example, during composting or incineration of polymeric waste. It can be concluded that this method can be used for various scientific, industrial and environmental applications, whenever fast determination of the kind and amount of volatile products formed during polymer degradation is needed. The method is straightforward and the instrumentation is very rugged and easy to use.

ACKNOWLEDGMENT

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WYNALAZKI

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Emalia piecowa (Zgłoszenie nr 326 987, Nobiles — Kujawska Fabryka Farb i Lakierów, Sp. z o.o., Włocławek)

Emalia piecowa na podstawie żywic alkidowych i żywicy melaminowej, zawierająca pigmenty, rozpuszczalnik oraz środki pomocnicze (np. poprawiające stopień zdyspergowania, rozlewność i odporność na sedymentację) charakteryzuje się tym, że zawiera (w cz. mas.) 17,85—23,15 żywicy akrylowej z grupą hydroksylową i, ewentualnie, karboksylową (najlepiej w postaci 60-proc. roztworu w mieszaninie octanu butylu, trimetylobenzenów i ksylenów), 11,59—15,60 żywicy alkidowej chudej na podstawie oleju rycynenowego (najlepiej w postaci 60-proc. roztworu w mieszaninie butanolu, trimetylobenzenów, etylotoluenów i ksylenów), 17,85—23,62 żywicy alkidowej na podstawie syntetycznych kwasów tłuszczowych (najlepiej w postaci 65-proc. roztworu w ksylenie i butyloglikolu), 16,26—19,70 średnio reaktywnej żywicy melaminowo-formaldehydowej (najlepiej w postaci 50-proc. roztworu w butanolu), 2,00—22,00 pigmentów i do 4,00 środków pomocniczych; resztę do 100,00 stanowią rozpuszczalniki (wg Biul. Urz. Pat. 2000, nr 1, 32).

Sposób wytwarzania aerozolu krzemionkowego (Zgłoszenie nr 327 295, Instytut Chemii Przemysłowej, Warszawa)

Alkoholowy roztwór alkoksysilanów poddaje się hydrolizie w środowisku kwaśnym, a następnie polikondensacji w środowisku zasadowym. Aerozol wytwarza się w postaci granulatu lub płyt, zwłaszcza do stosowania w budownictwie jako izolator cieplny (wg Biul. Urz. Pat. 2000, nr 2, 40).

Preparat uzdatniający włókna celulozowe, poliestrowe, poliamidowe bądź ich mieszaniny do sublimacyjnego druku transferowego (Zgłoszenie nr 327 382, Grzegorz Włodarczyk, Łódź i Wojciech Pałczyński, Warszawa)

Jako podstawowe składniki preparat zawiera produkty poliaddycji alkoholi wielowodorotlenowych (I) do izocyjanianów i/lub produkty polikondensacji I z kwasami dikarboksylowymi i/lub mieszaninę homo- i kopolimerów akrylowych (wg Biul. Urz. Pat. 2000, nr 2, 40).

J. F.