

Mechanism of photostabilization of perfluoropolyether coatings by hindered amine stabilisers

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Received 12 September 2000; accepted 1 January 2001

Abstract

Perfluoropolyethers show promising properties for coil coating application and a suitable layer is obtained by incorporating them in a crosslinked polyurethane network. However, photo-oxidative stability of urethane linkages is intrinsically low and an appropriate stabiliser must be added to the reactants prior to curing. The *N*-methyl HAS bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (Tinuvin765) has been selected for this model study. The chemical structure of the network strongly depends on the curing conditions: coil coating conditions (280 °C/1 min in air) lead to a polyurethane network also containing some urea-bridges and unreacted isocyanate. HAS further modifies the network increasing the urea-bridges at the expenses of the unreacted isocyanate. This kind of network is shown to be intrinsically more resistant to the photo-oxidation than pure polyurethane. In curing conditions the *N*-methyl HAS is partially transformed into –NH derivatives which are still active antioxidants. During photo-oxidation HAS acts as a radical scavenger but slowly evaporates from the film. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Perfluoropolyether derivatives; Fluorinated polyurethane; Photo-oxidation; HAS stabiliser

1. Introduction

Coil coating is a technology of ever increasing relevance in which simple manufactured goods such as bars and laminates are painted in a continuous process before being shaped into their final form. In fact, the coating of a flat laminate or of an unfolded bar is far easier and more successful than painting finished goods of complex shapes.

A suitable layer for coil coating application results from curing bi-functional OH derivatives perfluoropolyethers [1] and poly-functional isocyanates, obtaining a polyurethane network. This layer shows suitable properties both for the coating's industrial process and the product's final use such as flexibility, chemical resistance, surface properties and good adhesion to the primed metal strips. These high performances are related to the presence of fluorine chains, but the overall durability is limited by the hydrogenated blocks of the isocyanate, whose resistance

to the photo-oxidation is low. In effect, high durability of this coating in conditions of use is a compulsory requirement for their exploitation.

Thus, the hydrogenated regions represent the weak point to a rapid photo-ageing of the matrix. For this reason, stabilisation against photo-oxidation is strictly required and an appropriate stabiliser must be used. It must be added to the reactants prior to curing which, in this technology, occurs in relatively severe conditions, in order to be effective in the short time offered by a continuous process.

Hindered amine stabilisers (HAS) are known to be very effective antioxidants. The mechanism by which they act is still a matter of discussion but it is nowadays widely accepted that the amine functionality is converted to the stable nitroxyl radical in the very first steps of oxidation in the presence of oxygen and hydroperoxides. It is the nitroxyl radicals that scavenge the very reactive alkyl radicals.

The product of this reaction is able to react with peroxy radicals reforming the original nitroxyl radical [2]. The self-sustaining cycle established in this way is

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responsible for the high effectiveness of HAS. As far as HAS structure is concerned, sufficient mobility has been shown to be the key factor for an efficient photo-protection [3]. In effect, the scavenger must be able to capture the incoming radicals as soon as and where they are formed; for this reason very high molecular weight HAS or in-network HAS, which have the advantage of not being leached out from the coating layer, show poor effectiveness. However, the degree of photo-protection achieved in the stabilised coil coating system is still lower than that obtained for a corresponding system cured in milder conditions [3].

The aim of this paper is to investigate the mechanism of both photo-oxidation of the above system and photo-protection imparted by the selected HAS.

2. Experimental

2.1. Materials

OH bi-functional perfluoropolyethers (Fluorobase Z 1031, Ausimont) of M_w 1200 and an isophoron-diisocyanate (IPDI) trimer (Vestanat B 1358/A, Huls) were used as a co-monomers. The $-NCO$ functional group of IPDI trimer was ketoxime end-capped but the original functionality can be restored by simple heating.

The commercial HAS Tinuvin 765 (Ciba Specialty Chemicals) was selected because of its relatively high mobility, low basicity and good compatibility with polyurethanes. Low basicity is required to reduce interactions with the acid catalyst. The formal structure of Tinuvin 765 is bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate but GC/MS analysis (see below) shows that it also contains 15% of the low molecular weight precursor methyl-(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate.

2.2. Film preparation

The reactants were mixed using a 15% excess of $-NCO$. This is necessary for compensating the high reactivity of isocyanate. The mixture was spread on a glass support using 20 μm roller bars and the film cured in coil conditions (280 $^\circ\text{C}/55$ s in air); using 0.4% of dibutyltin dilaurate as a catalyst ($\text{C}_{23}\text{H}_{64}\text{O}_4\text{Sn}$, $M_w = 631.56$, $d = 1.05$). A stabilised network containing 3% of HAS was also prepared in the same conditions. For comparison purposes an unstabilised film cured in milder conditions (150 $^\circ\text{C}/1$ h) was also prepared.

2.3. Film ageing

Photo-ageing was carried out in SEPAP 12/24 equipment ($\lambda > 295$ nm). The samples were exposed to the light directly as self-supporting films ready for IR study or in strips in open EPR quartz tubes for EPR investigation.

Careful calibration was carried out to evaluate the effect of the presence of the tube on the kinetics of ageing.

2.4. Techniques

IR spectra were run on a Perkin Elmer 2000 FTIR on self supporting films. Spectra were normalised to the band at 687 cm^{-1} due to C–F absorption which is stable to photo-oxidation. Grams 2000 software (Galactic Industries Corporation) was used to perform mathematical separation of overlapping bands.

GC–MS experiments were performed on a HP 5890 GC coupled with a MS quadrupole detector HP5970. The stabiliser was extracted from the freshly cured film by soxhlet extraction in hexane for 24 h. Quantitative analy-

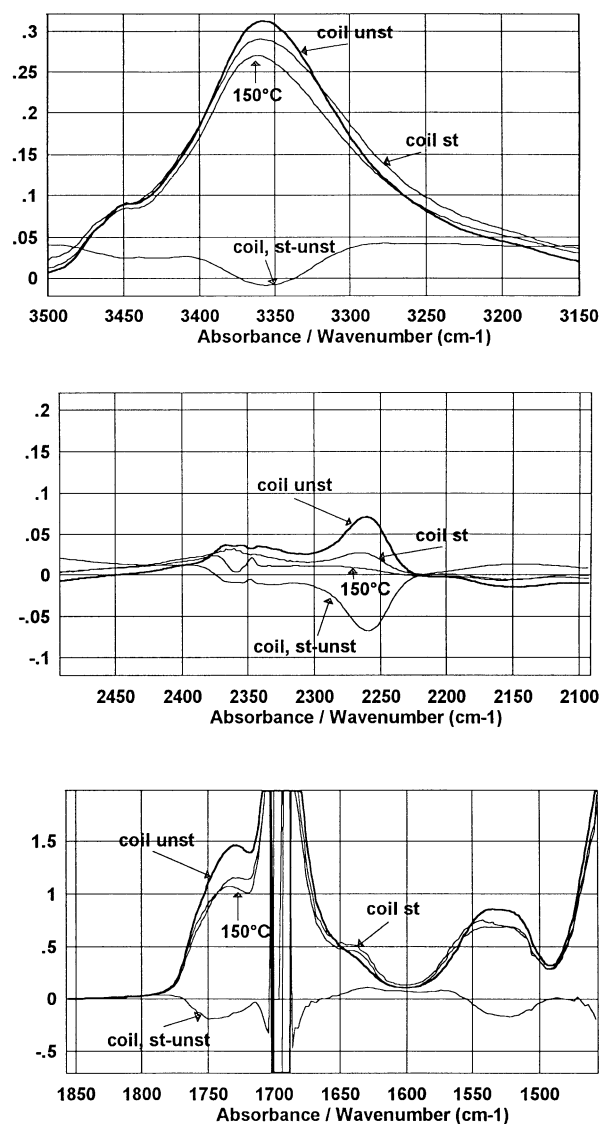


Fig. 1. IR of unstabilised film cured at 150 $^\circ\text{C}/1$ h; of unstabilised and stabilised film cured in coil coating conditions and their difference (stabilised–unstabilised).

sis was carried out on the appropriate ion of the MS spectra using isopropyl benzene as an internal standard.

EPR was run on a Bruker ESP 300E on strip samples. Quantitative analysis was performed by calibration using known volumes of nitroxyl radical water solution.

Exposure of the samples to trifluoroacetic acid vapour was carried out to quantitatively convert the $-NH$ form of the stabiliser into nitroxyl radicals suitable for EPR investigation [4].

3. Results

3.1. Network structure

$-NCO$ is a very reactive group and the final network contains different structures depending on the curing conditions. The main possible products are:

- urethane bridges ($-NCO + -OH$)
- $-NH_2$ end groups and CO_2 ($-NCO + H_2O$)
- allophanates ($-NCO +$ urethane)

in addition urea bridges ($-NH_2 + -NCO$) and biuret (urea bridges $+ -NCO$) can be also formed.

IR spectra (Fig. 1) show that introduction of the HAS in the system modifies the network structure by increasing the urea-bridges ($1635, 1566, 3350\text{ cm}^{-1}$) [5] to the detriment of urethane bonds ($3360, 1740, 1540\text{ cm}^{-1}$) [5], and of unreacted isocyanate (2260 cm^{-1}) [5]. The amount of urea bridges in the unstabilised film cured at $150\text{ }^\circ\text{C}/1\text{ h}$ is similar to that of stabilised coil-cured film.

GC-MS analysis (Fig. 2) shows that during the severe conditions of the coil-coating curing the *N*-methyl HAS is partially transformed into $-NH$ HAS derivatives. In addition most of the low molecular weight impurity volatilises. Quantitative results show that after curing

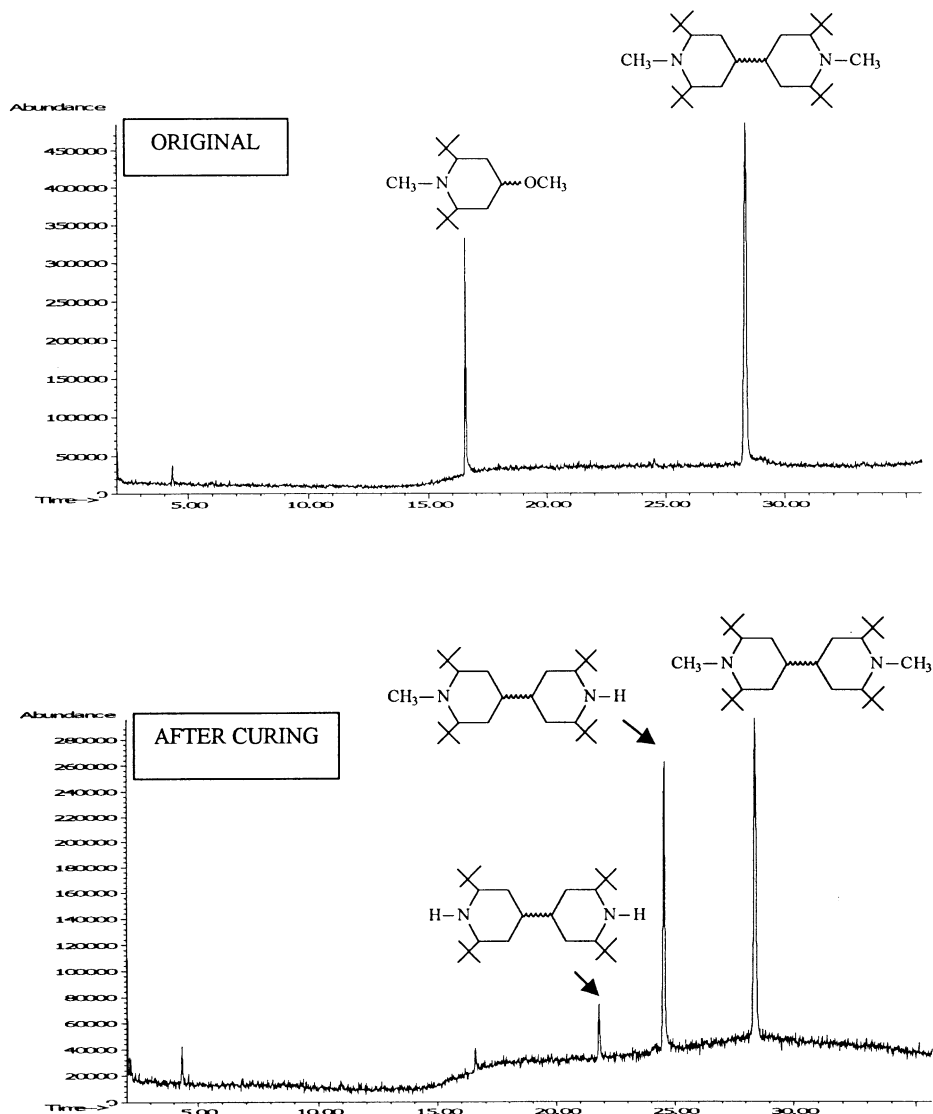


Fig. 2. Total ion current chromatogram of original stabiliser and of that extracted from the film after curing.

the stabiliser mixture contains 1% of low molecular weight impurity, 46% of original di-N-CH₃ derivative, 24% of di-NH derivative and 29% of -NH-NCH₃ derivative.

EPR spectra of the original cured sample show that 0.3% of the initial stabiliser is converted to nitroxyl radical.

3.2. Network ageing

Visual inspection shows that, upon photo-oxidation, the films retain their mechanical integrity for different times; namely up to 1300 h for stabilised coil-cured film, up to 1800 h for unstabilised 150 °C cured film and up to 2000 h for the stabilised coil-cured film.

The structure variation on ageing has been followed by monitoring the IR absorption in the 2900 and 1550 cm⁻¹ range. The first refers to the aliphatic CH₂ and CH₃; the second to urethane and urea bridges. In photo-oxidation CH₂ groups are converted to carbonyl. During photo-ageing both these absorptions decrease (Fig. 3a and b). The rate at which functional groups disappear is slowed in stabilised films. In addition the urea-bridges

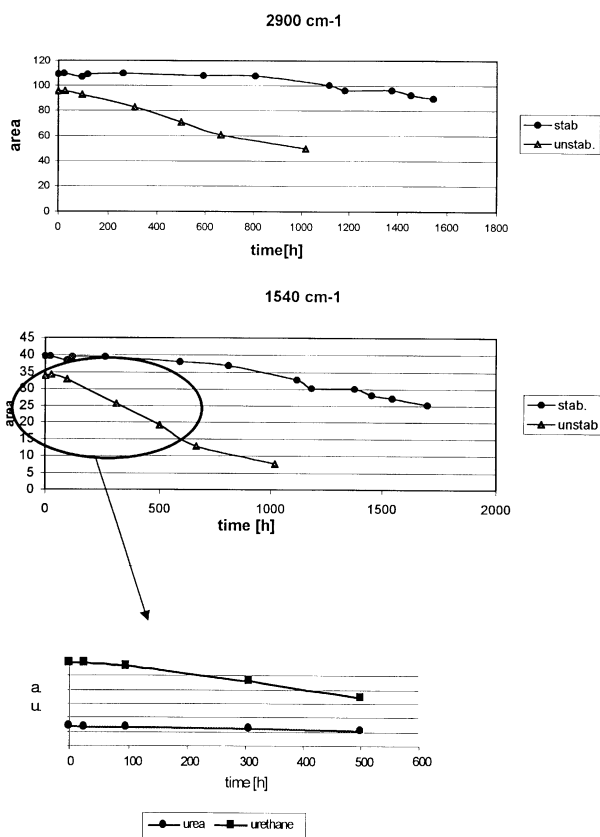


Fig. 3. Photo-oxidation kinetics of urea and urethane bridges at $\lambda > 295$ nm in films 280 °C/55" (coil conditions). (a) 2900 cm⁻¹ band (area); (b) 1540 cm⁻¹ band (area); (c) 1540 cm⁻¹ band (computer separation of overlapping contributions of urea and urethane structure to that band).

are intrinsically more resistant to the photo-oxidation than pure urethane (at $\lambda > 295$ nm) [6] as shown in Fig. 3c for unstabilised film.

During ageing, new functional groups are formed, either in unstabilised or stabilised films, but obviously at a different rate (Fig. 4). The main new functionalities are:

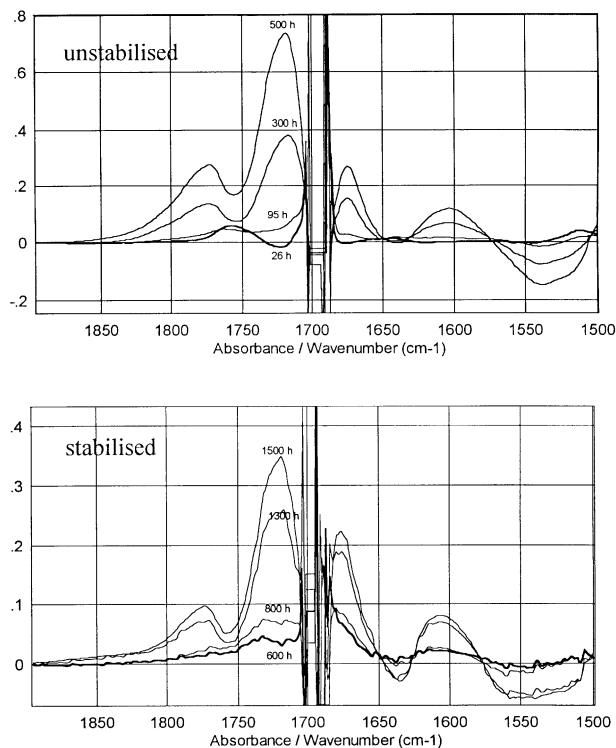


Fig. 4. IR differences (aged-original) of unstabilised (upper) and stabilised films (bottom) for different times of ageing.

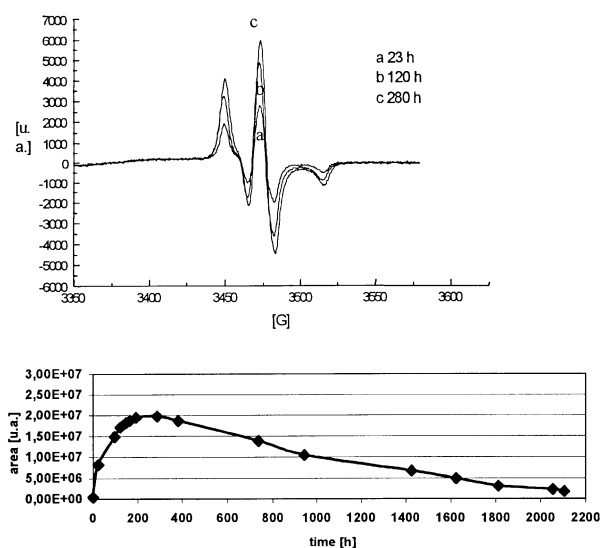


Fig. 5. (a) ESR spectrum of nitroxyl radical upon photo-oxidation. (b) Nitroxyl radical kinetics in films added with 3% HAS, during exposure at $\lambda > 295$ nm.

- acylurethane (1755 cm^{-1}) [7] are formed (26 h of ageing) and then consumed
- carbamates ($3300, 1720, 1680, 1607\text{ cm}^{-1}$) [5]
- acids whose absorption in 1700 cm^{-1} range overlaps other bands and have been confirmed by SF_4 derivatisation.

This means that the same mechanism of ageing is established in both samples. However, in stabilised films HAS, because of its relatively high mobility, is able to trap the radicals progressively created in the system reducing the rate of photo-ageing without changing the mechanism.

3.3. Stabiliser fate

Nitroxyl radical derivatives formed from HAS oxidation are very long-lived species, especially in a solid matrix, and can be easily detected by ESR. (Fig. 5a). Thus, the in situ concentration of nitroxyl radicals has been monitored as a function of ageing time (Fig. 5b). Quantitative analysis was done through a calibration [6]. Upon irradiation the nitroxyl radical concentration is found to increase from 0.3 wt.% to a maximum at 300 h. The conversion of HAS into nitroxyl radical is ca. 15 wt.% of total HAS. From this point on the HAS concentration slowly decreases and eventually fades away at 1700 h; at this time there is no more extractable stabiliser in the film. Slow evaporation of stabiliser thus occurs during ageing.

4. Discussion

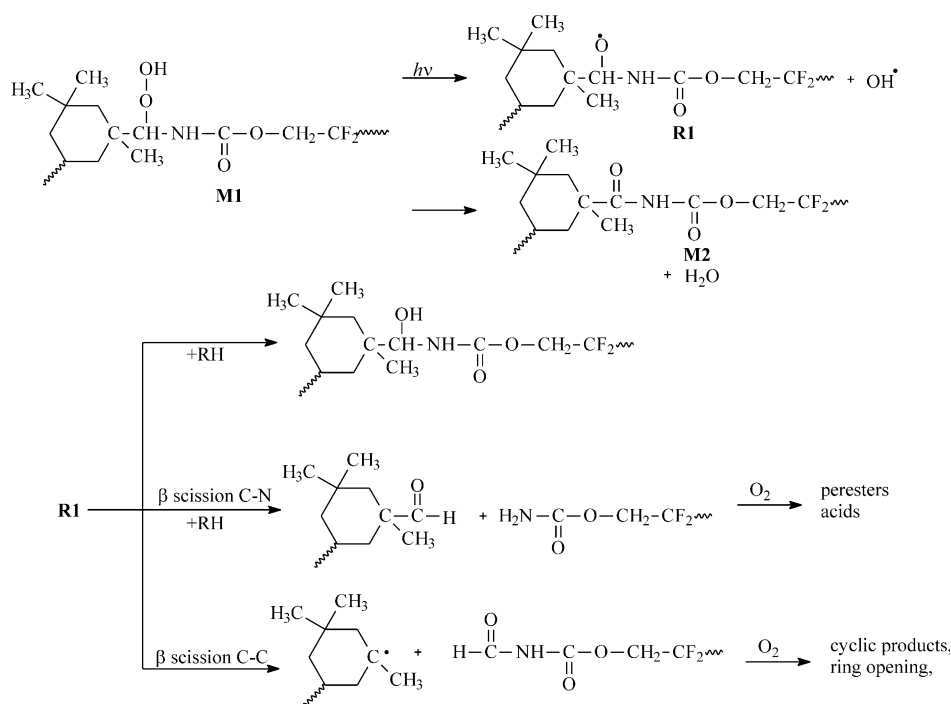
4.1. Network structure

The severe coil coating curing conditions lead to a network relatively poor in urea bridges. Urea formation is favoured by basic ambient conditions and longer reaction times [8]. These films have been cured using an acid catalyst for a very short time, thus this finding is not surprising. However, the introduction of a stabiliser increases the amount of urea bridges because it increases the basicity of the reaction system. In effect, despite the tertiary amine introduced in the system, the curing condition favours its partial conversion to secondary more basic amine as shown by GC data.

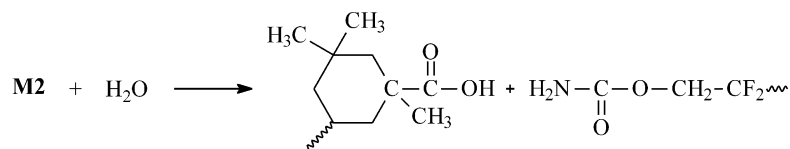
4.2. Photo-oxidation mechanisms

Because of the protection effect of the nitrogen atom, the attack site is the $-\text{CH}_2-$ α to the nitrogen which will be easily peroxidised (**M1**) by atmospheric oxygen. Formation of alkoxy radical **R1** or of acyl urethane **M2** are possible. The fate of the radical **R1** is to form hydroxy derivatives, peresters, acids, ring and ring-opening products as depicted below (Scheme 1). Spectroscopic evidence for most of these products has been shown.

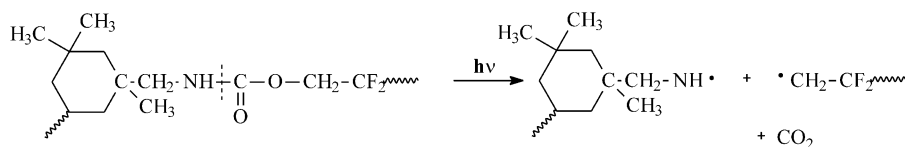
M2 can form carbamates and acids by hydrolysis. Water can be that of the atmosphere but also that formed in situ (Scheme 2).



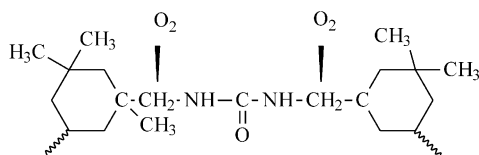
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Direct photolysis of urethane is also possible (Scheme 3) which leads to carbamate and acid for further oxidation

A similar product can be obtained from photo-oxidation of urea bridges, taking in account that they link two hydrogenated molecules and, therefore, there are two positions of oxygen attack. Scheme 4.

4.3. Photo-oxidation resistance

Stabilisation increases the photo-oxidative stability of the system from 1300 to 2000 h of accelerated ageing in the films cured according to the coil coating conditions. Stabilisation is improved by two mechanism:

1. HAS action as a radical scavenger
2. Increased amount of urea bridges.

Whereas factor 1 is well known, factor 2 needs some additional comments. Despite its two $-\text{CH}_2-$ groups α to the nitrogen, a network containing some urea bridges seems to be more resistant to the photo-oxidation. In fact, polyurethane films of the same composition but cured in milder conditions (150 °C/1 h) in effect show

relatively high urea content and photo-resistance up to 1800 h without addition of a stabiliser (Fig. 1). Thus, in the fluorinated system the presence of urea bridges is accompanied by improved photo-oxidative stability. Urea bridges link two tri-functional isocyanates instead of one tri-isocyanate and one bi-functional fluorinated molecule, therefore the density of crosslinking increases leading to a more interconnected network. This increases the mechanical stability of the coating because it requires more scission to form volatile fragments. In addition, oxygen diffusion should be in some way hindered in this tight network reducing the overall rate of photo-oxidation.

References

- [1] Sianesi D, Pasetti A, Fontanelli R, Bernardi GC, Caporiccio G. *La Chimica e l'Industria* 1973;55:208.
- [2] Zweifel H. *Stabilisation of polymeric materials*. Berlin: Springer-Verlag, 1998.
- [3] Novelli S, Turri S, Luda MP, Camino G, et al. *Proceedings of XIV Convegno Italiano di Scienza e Tecnologia delle Macromolecole* 1999;1:243–6.
- [4] Commereuc S, Schiers S, Verney V, Lacoste J. *J Appl Polym Sci* 1998;69:1107–14.
- [5] Hummel O, Scholl F. *Atlas of polymer plastics analysis*, vol. II part b1. New York: C. Hanser, 1988.
- [6] Vaccarone P. Degree thesis University of Torino, Academic Year 1998–1999.
- [7] Wilhelm C, Gardette JL. *Polymer* 1997;38:4019–31.
- [8] Lenz RW. *Organic chemistry of synthetic high polymers*. New York: John Wiley Interscience, 1967.