Progress in Organic Coatings 40 (2000) 93–97

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

New UV curing systems for automotive applications

K. Maag [a,*], W. Lenhard [b], Helmut Löffles [b]

[a] *Ciba Specialty Chemicals Inc., Schwarzwaldallee 215, CH-4002 Basel, Switzerland*
[b] *DuPont Performance Coatings, Christbusch 250-42285 Wuppertal, Germany*

Abstract

Recent developments of new UV curable resins, which meet the high demands of automotive applications (e.g. weather stability), in combination with a new lamp technology offer extremely fast drying of paints, giving complete curing within less than 2 min (in some cases even within seconds). Since the capacity of the painting/drying booth is the bottleneck in most body shops and OEM lines, this new technology offers a remarkable time saving advantage to the customer. The new technical standard is presented by a dual cure system due to the advantages of lower volume shrinkage and curing of shadow areas. The change of mar and chemical resistance depending on the amount of UV curable components in a one pack automotive clear coat is shown. The influence of both — temperature and distance — between the lamp and the painted object has been investigated by the decrease of UV curable double bonds in a given dual cure refinishing clear coat.

Keywords: UV flash technology; Automotive applications; UV curable coatings; Refinishing

1. Introduction

UV curing systems are not really new. The economic feasibilities of UV curing systems have been successfully approved in other industrial businesses like wood paints and printing inks. But for automotive applications in OEM as well as in refinishing business raw materials, e.g. binders and reactive monomers with excellent weathering resistance were not available until now. The combination of new raw materials with a brand-new UV flash technology, easy to handle, transportable and safe, now provides a big step forward especially for the automotive refinishing applications. Anyway, the resulting film properties as well as appearance have to satisfy the high quality demands of the customer.

However, using 100% UV curable systems even in the case of clear coats surface cracks occurred depending on curing and storage conditions after curing, due to the volume shrinkage and curing gradient especially on black or dark base coats.

It seems that the approach to combine the UV curing system with a second cross linking chemistry — usually OH functional resins like acrylic acrylates with conventional cross linkers, e.g. NCO and/or NCO functional acrylic acrylates (Fig. 1) or the combination of UV curing binders with conventional curing system, e.g. one pack alkyd melamine (OEM) — solves this problem. The conventional curing part plasticises the rigid network of “UV-binders” and lowers cross linking density. As an additional advantage non-curing of 100% pure UV curing mixtures in shadow areas could be avoided. Both dual cure systems have been investigated. The results are shown and discussed below.

2. Curing equipment and curing mechanism

The applied curing equipment is based on UV flash technology. The full cure occurs within extreme short time as mentioned before. The high energy and intensity of the UV flash (Xe lamp, Fig. 2) is generated by an electrical discharge of a capacitor and depends on its capacity and the resulting lamp temperature. The time lag between charging and discharging is about 4 s. Of course the curing time needed (number of flash lights) is a function of the electrical equipment properties, reactivity of the resins, pigmentation and film thickness, the distance between object and the lamps as well as the object temperature. The distribution of light which has to be homogenous is another important influence on the curing results (Fig. 3). Therefore, a special reflector geometry is required for three-dimensional objects.

In addition a photoinitiator is needed for the UV curable part of the mixture. This initiator is stimulated by UV radiation and produces reactive radicals which initiate the polymerisation of resins with unsaturated double bonds such as polyurethane acrylates, acrylic acrylates, etc. (Figs. 4 and 5). The NCO/OH reaction, e.g. occurs during IR heating

* Corresponding author. Tel.: +41-61-637-8238; fax: +41-61-637-5627.
E-mail address: karin.maag@cibasc.com (K. Maag).

0300-9440/00/$ – see front matter
PII: S0300-9440(00)00144-2

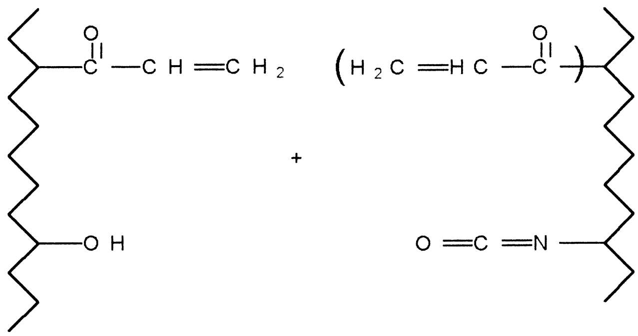

Fig. 1. Example for dual cure cross linking mechanism.

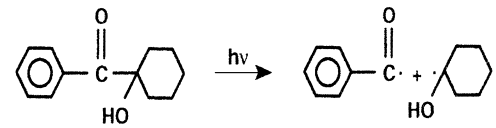

Fig. 4. Light induced cleavage of α-hydroxy acetophenone.

before UV curing and continues reaction later on by room temperature. The IR lamps are integrated in the reflector of the UV curing equipment. Best results are obtained in the mixture of one pack alkyd melamine and UV curable resins when the UV curing takes place first, whereas the drying of the conventional part occurs later on in the oven at 145°C.

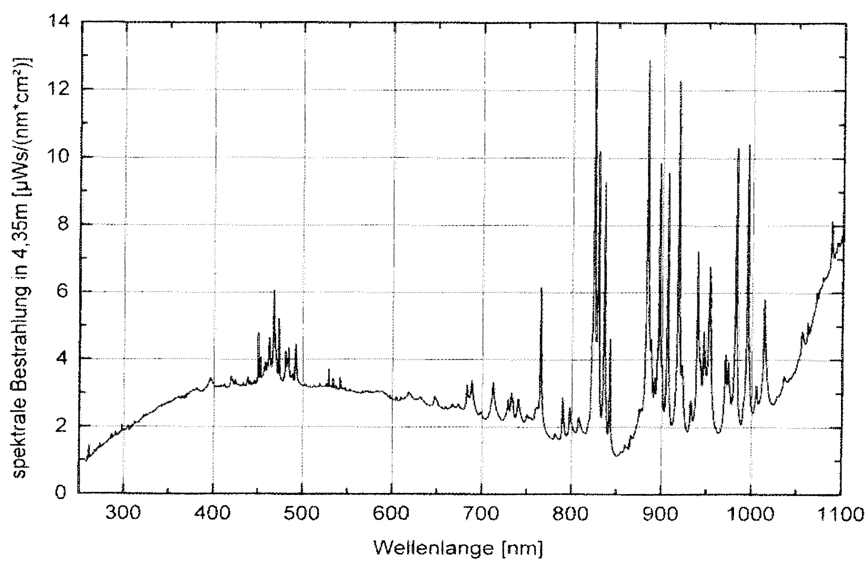

Fig. 2. UV spectrum of the Xe-flash lamp.

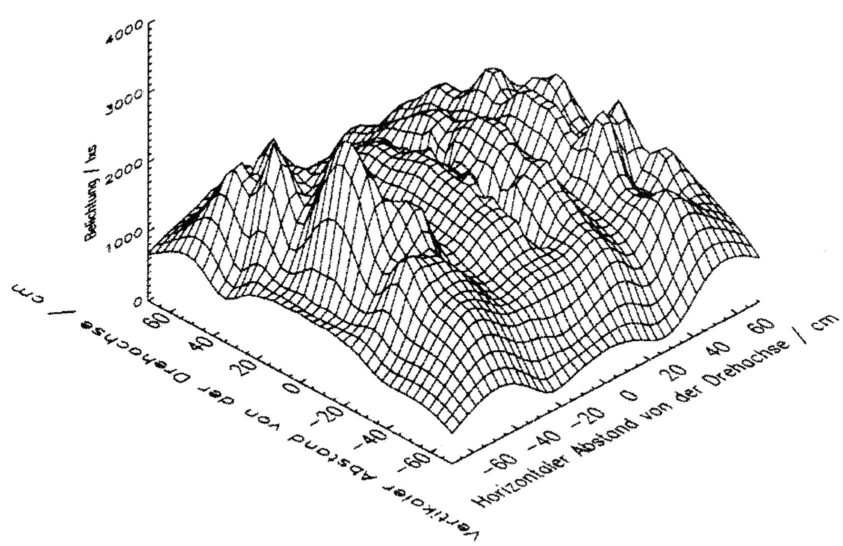

Fig. 3. Homogenous light distribution due to a special reflector geometry.

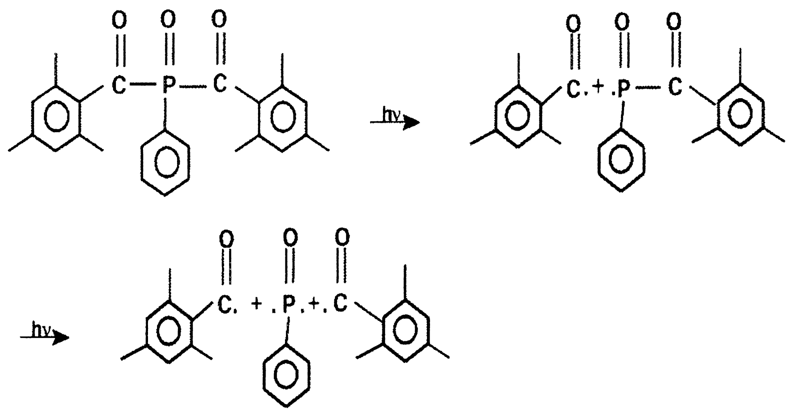

Fig. 5. Light induced cleavage of bis-acyl-phosphine-oxyd.

3. Results and discussion

3.1. Refinishing

A combination of an OH functional acrylic acrylate with an NCO functional hardener (mixing 2:1) is used for this purpose. The mixture includes also the commonly used light stabilisers as well as solvents and slip agents. The influence of both temperature and distance between the lamp and the curing object on the decrease of UV curable double bonds in the dual cure system with a given amount of UV curable components has been investigated by Raman spectroscopy.

All test panels ($20 \times 30\,cm^2$) were prepared in the same manner. The flash-off time before IR drying was about 5 min at room temperature followed by 5 min IR 40 or 60°C. Afterwards the UV curing takes place. The resulting clear coat film thickness was 50 μm.

In Fig. 6 the decreasing UV curable double bonds with increasing number of flashes and the influence of the object temperature is shown. In each case (20, 40 and 60°C) the decrease of double bonds with increasing flashes is approximately exponential.

With increasing number of flashes the positive effect of the higher temperature is neglected, although at higher temperatures the needed energy input is lower which entails shorter curing time. In addition higher temperature is needed before UV curing to accelerate the second curing mechanism (e.g. OH/NCO reaction) especially in the non-cured shadow areas.

This correlates with the results of mar and chemical resistance tests. Only at higher temperature (40 and 60°C) and number of flashes (above 10) the test results also in shadow areas are acceptable due to the higher network density of the resulting films. In comparison to the common two pack polyurethane clear coat the film properties of the dual cure system are improved especially directly after curing. However, no difference in resulting film properties could be detected between the panels which are cured with 10 and 20 flashes due to the insensitivity of the measuring methods. The variation of the distance between the lamp and the

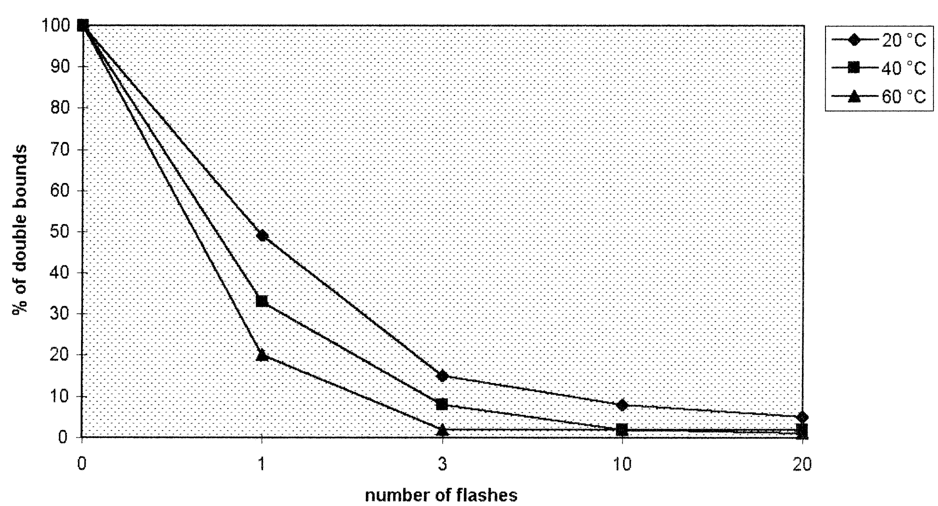

Fig. 6. Decrease of double bonds in dependence of temperature and number of flashes, distance between lamp and object = 20 cm.

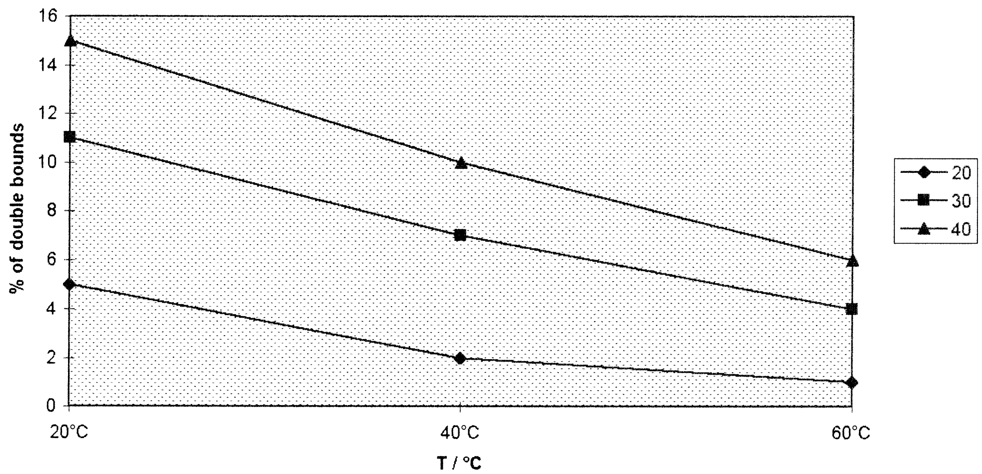

Fig. 7. Decrease of double bonds in dependence of the distance between lamp and object (cm), number of flash lights = 20.

curing object has the same effect which is shown in Fig. 7. The decrease of double bonds by constant flash numbers is approximately linear to the variation of distance.

3.2. Automotive

The change of mar and chemical resistance depending on the amount of UV curable components in a one pack alkyd melamine automotive clear coat has been investigated. The UV curable components were a mixture of a hexa functional polyurethane acrylate, TMPTA and a photoinitiator (75:22:3). The concentration of the UV curable mixture has been varied between 3 and 65% in accordance with the one pack alkyd melamine solid content of 50%. The standard was the normal one pack alkyd melamine. Since the application conditions in automotive lines are different from those in refinishing applications the film thickness of the clear coat has been reduced to 35 μm. As mentioned before best results in this case has been obtained when the UV curing part takes place before heating the panels in the oven (20 min, 145°C). The number of flashes in each case was 10.

The chemical resistance has been detected with the xylene test and the determination of the pendulum hardness before and 10 min after the test. The mar resistance has been measured with the "Peters Klotz" method and the gloss before and after strain has been ascertained. The results are given in Figs. 8 and 9.

The resulting dual cure clear coats show a very good chemical resistance. With increasing content of the UV mixture the pendulum hardness before xylene test increases up to a maximum value of 121 (at 65%) which corresponds to a chemical resistance improvement of 30% in comparison to the standard. Unfortunately the flexibility of the film decreases in the same direction. Therefore the optimum content of UV curable components in the one pack clear coat lies between 20 and 45%.

All mixtures showed an excellent self healing behaviour after the xylene test. In each case complete regeneration

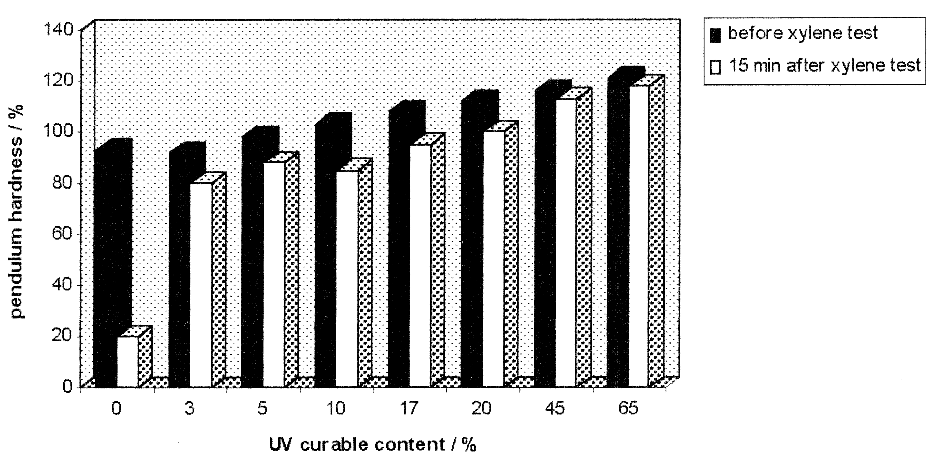

Fig. 8. Pendulum hardness in dependence of UV curable content (%) before and 15 min after xylene test.

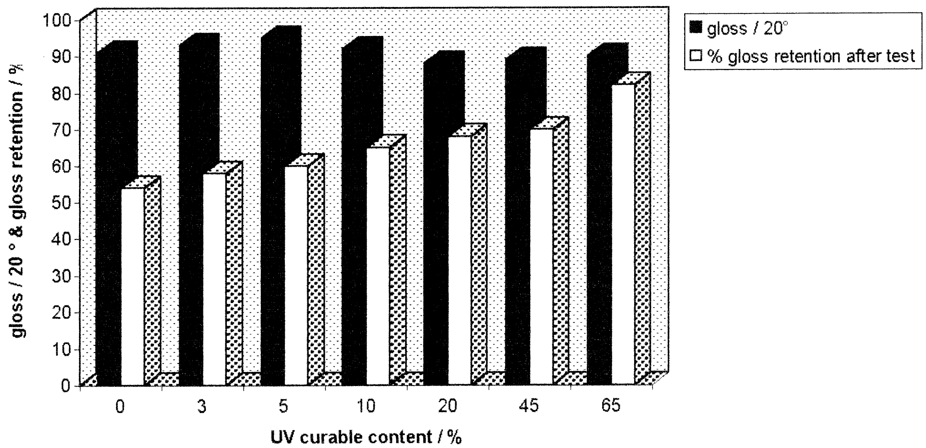

Fig. 9. Gloss and gloss retention after Peters Klotz in dependence of the UV curable content (%).

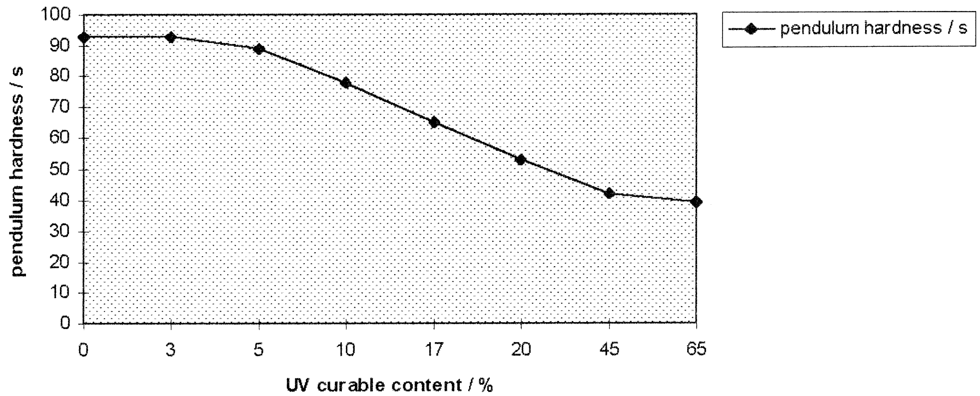

Fig. 10. Pendulum hardness in shadow areas in dependence of the UV curable content (%) (only oven curing 20 min, 145°C).

of the film properties has been determined after 15 min approximately. In contrast the standard embodies a very poor chemical resistance (see Fig. 8, 0% UV curable content). The results of chemical resistance correlates with the mar resistance examination (see Fig. 9). The addition of the UV mixture has no influence on the gloss/20° and improves the mar resistance dramatically. Taking into account that a UV curable content higher than 45% reduces the film flexibility and also has a disadvantageous effect on the curing behaviour in shadow areas, which is shown in Fig. 10, the optimum UV curable concentration is about 20–40%.

4. Conclusion

The first positive results of the investigated dual cure systems have shown that this new technology will enable a new pathway for automotive refinishing as well as for automotive applications to improve the properties of commonly used solvent borne clear coats. The development of a pigmented filler is in preparation. Further developments will be necessary especially tailor made resins to receive optimal properties of dual cure systems. In accordance to the new VOC guidelines further development has to focus on water borne systems.

Further reading

R. Königer, et al., Farbe and Lack 105 (4) (1999) 233.
D. Skinner, PPCJ (May 1999) 21.
N.S. Allen, et al., Surf. Coat. Int. 2 (1999) 67.
A. Valet, in: Proceedings of the XXIVth International Conference in Organic Science and Technology, Athens, 1998, p. 427.