

**DETERMINATION OF SOME PHYSICO-MECHANICAL
PROPERTIES OF AQUEOUS TWO-COMPONENT VARNISH
PAINTS BY USE OF NON-TIN CATALYSTS**

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Abstract. *In last several years the use of water instead of organic solvent in coating paints has increased considerably. It is the consequence of the increasingly severe demands for environmental protection as well as of the efficiency of aqueous coatings in the protection of materials by means of organic coatings. The main aspect in developing the aqueous two-component polyurethane (PU) systems is, first of all, finding methods for preventing unwanted secondary reactions with water and obtaining the best crosslinking.*

In this paper, the polyol components, as well as the acrylic dispersions with different hydroxyl numbers for crosslinking process, were used.

As suitable hardeners, the aliphatic polyfunctional isocyanates based on hexamethylen diisocyanates with different content in the NCO-group were used. In this study, the complex of zirconium commercial known as K-KAT[®]XC-6212 or manganese (III) complex with mixed ligands based on the derivative of maleic acid was used as the catalyst. The coatings were characterized by measurements of hardness by König and gloss by Lange using catalysts with different selectivity. In this respect, the effect of different induction times after the mixing of the components on the hardness and gloss of the films has also been observed.

The obtained results show that the performances of the aqueous two- component polyurethane coatings depend on the polymer structure of the polyols and the polyisocyanates as well as on the selectivity of the used catalyst.

Key Words: *Aqueous coatings, crosslinking, induction time, hardness according to König*

INTRODUCTION

In past several years, the use of water instead of organic solvents in coating agents has increased highly. It is the result of the increasingly severe demands for environmental protection, as well as of the efficiency of aqueous coatings in the protection of materials by means of organic coatings.

Since aqueous coatings are accepted more and more, and as new technologies are being employed, research is directed toward the development of aqueous coatings that could be accepted for use in difficult environmental conditions. Consequently, research on the aqueous two-component coatings indicates that they can withstand strains that are set in rough exploitation conditions.

The basic principle with two-component polyurethane coatings is a high reactivity of the isocyanate group of the polyfunctional isocyanate that reacts easily with hydroxyl polymer groups, thus forming stable polyurethanes and creating a transversal binding structure [1]. If the system contains water, then the reaction of the isocyanate group with water leads to the occurrence of the primary amine and further to the formation of polyurea with a simultaneous evolution of carbon dioxide. The reactions with water are not desirable because isocyanate groups that react with water are not available for crosslinking with polyol, and the created carbon dioxide can be captured in the form of bubbles in the dry film.

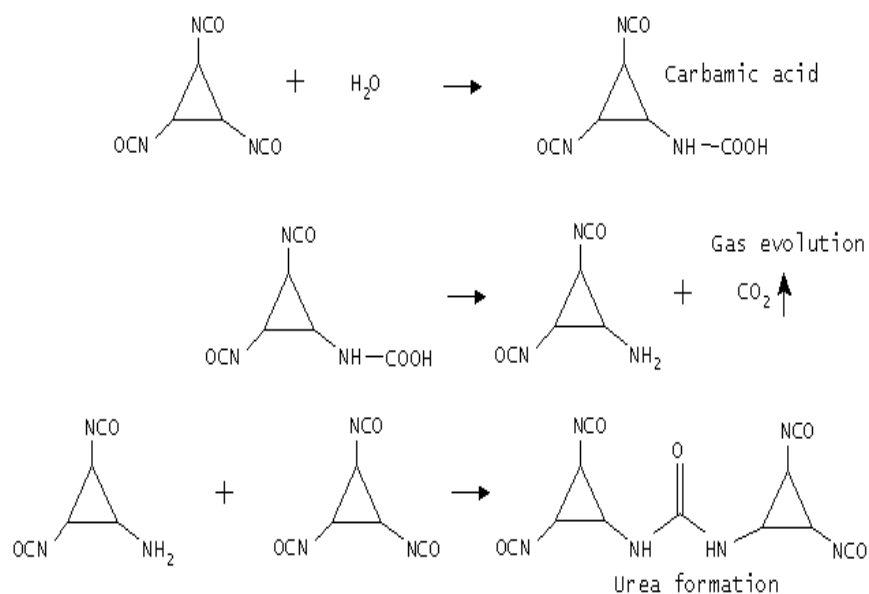


Fig. 1. Reactions of isocyanates with water

The main aspect in the development of the aqueous polyurethanes is, in the first place, to find methods for preventing the undesired secondary reactions with water and for achieving the best crosslinking. This reaction is reduced to a minimum by the use of non-tin catalysts.

In the research of Werner Blank [2], the selectivity of various compounds to model compounds was examined. Butyl isocyanate and 2-ethyl-1-hexanol were selected as model compounds because their similarity with aliphatic polyisocyanates and hydroxyl resins as well as because of the simplicity of their FTIR spectra. We have examined the following as catalysts: compounds of octonates of Zn, Co and Mn, acetylacetonates of Co, Zn, Ni, Al and Mn (Merck-Schuchardt), the catalyst of zirconium designated K-KAT[®]XC-6212 (King industries, Norwalk-USA), as well as the complexes of manganese with various ligands.

The relation of the surface of IR urethane strips (P_{urethane}) to urea (P_{urea}) was used as the measure of the relative selectivity (S).

$$S = P_{\text{urethane}} / P_{\text{urea}} \quad (1)$$

The manganese complex with various ligands based on the derivatives of maleinic acid [3] that was used in the experiment, in our research showed a high selectivity for the isocyanate-hydroxyl reaction.

The effect of the catalysts of different selectivity was observed in the research indirectly, by measuring the mechanical-optical parameters of the formed films.

EXPERIMENTAL PART

In the first part of the experimental program, the two polyol components, acrylic dispersions with the hydroxyl number 100, were used, and they are: Luhydran LR 8833, with the lowest temperature of film forming of 308 K and Luhydran LR 8845, with the lowest temperature of film forming of 333 K.

Three kinds of water emulsible polyisocyanates on the basis of hexamethylen diisocyanate were applied as suitable crosslinkings: Basonate PLR 8878 (17-18 % NCO), Basonate PLR 8901 (13.5-14.5 % NCO), Basonate PLR 8963 (18.5-21.5 % NCO).

Two polyol components with a hydroxyl number above 130 used in the second part of the experiment are: an acrylic dispersion in the water/butyl alcohol mixture, (Macrynal VSM 2521 w/42 WAB, Solutia Austria GmbH) and also acrylic resin as water dispersion (Macrynal VSM 6299 w/42 WA, Solutia Austria GmbH). The content of dry matter with these dispersions is 42%.

As suitable hardeners for these dispersions, the aliphatic polyfunctional isocyanates based on hexamethylen diisocyanates were employed and they are as follows: Bayhydur VP LS 2319 (18.2 % NCO), Bayhydur VP LS 2336 (16.2 % NCO), Bayhydur VP LS 2150 (13.4 % NCO) as well as Desmodur 3600 (23% NCO), Bayer AG Germany). The catalyst with a concentration of 2 % relating to the coating hardness was added after a certain period of induction time.

The determining of the hardness of the varnish paint films was carried out using the method (JUS H. C. 8.055), which requires the determination of hardness in an indirect way by measuring the time during which the oscillation amplitude of the pendulum leaned against the polymer dry film becomes smaller.

Apart from measuring the hardness, the change of gloss of the dried films was also examined using the method described by Dr Lange.

The Tables 1, 2 and 3 show the composition of the employed components.

Table 1. Two-component PUR compositions based on polyols: Luhydran LR 8833 and Luhydran LR 8845 and on hardeners: Basonate PLR 8878, Basonate PLR 8901 and Basonate PLR 8963.

Component A, Mass %	PUR 1	PUR 2	PUR 3	PUR 4	PUR 5	PUR 6
Luhydran LR 8833	89.6	89.6	89.6	–	–	–
Luhydran LR 8845	–	–	–	84.9	84.9	84.9
Buffer	0.9	0.9	0.9	0.9	0.9	0.9
Koalescent	5.4	5.4	5.4	5.4	5.4	5.4
Foam-removing agent	0.6	0.6	0.6	0.6	0.6	0.6
Component B Mass %						
Basonate PLR 8878	4.1	–	–	5.2	–	–
Basonate PLR 8901	–	4.1	–	–	5.2	–
Basonate PLR 8963	–	–	4.1	–	–	5.2
Total mass of components	100.6	100.6	100.6	97.0	97.0	97.0

Table 2. Two-component PUR composition based on polyol Macrynal VSM 6299 w/42 WA (coating hardness 52.5 %)

Component A , mass %	PUR 7
Polyol VSM 6299	65.13
water	8.6
Component B, mass %	
Bayhydur VP LS 2319	13.02
Dezmodur N 3600	8.6
Methoxypropyl acetate	4.3
Catalyst	2 % related to coating harness
Total mass of components	99.5

Table 3. Two-component PUR composition based on the polyol Macrynal VSM 2521 w/42 WAB (coating hardness 40.4 %)

Component A, mass %	PUR 8
Polyol VSM 2521	56.2
Water	22.6
Component B, mass %	
Bayhydur VP LS 2336	9.8
Bayhydur VP LS 2150 BA	9.8
Methoxypropyl acetate	1.1
Catalyst	2 % related to coating hardness
Total mass of components	99.5

PRESENTATION AND DISCUSSION OF THE RESULTS

Upon the application of the polyurethane dispersions on a substrate – glass plates, the process of drying and crosslinking takes place and consists of something in the evaporation of the present solvent and water and also in the reactions of the hydroxyl groups from the polyol and the isocyanate groups from the polyisocyanates.

In order to evaluate the behavior of the potlife, the coating can be observed visually (gas formation, viscosity change, coagulation). While the conventional two-component PUR systems show a stable viscosity increase, the aqueous two-component PUR coatings lack the reliable ratio between the viscosity increase and the potlife. Well stabilized aqueous coatings can behave almost without change in regards to viscosity and the very appearance because the greater part of the reactive groups of hardeners has already reacted. Therefore, the coating was applied onto the glass immediately upon being mixed with the hardener, then after two and four hours of induction time [4].

As regards to the low values of hardness that had been obtained with these polyol components (Fig. 2), further examinations were carried out with the polyols whose OH-numbers were above 130.

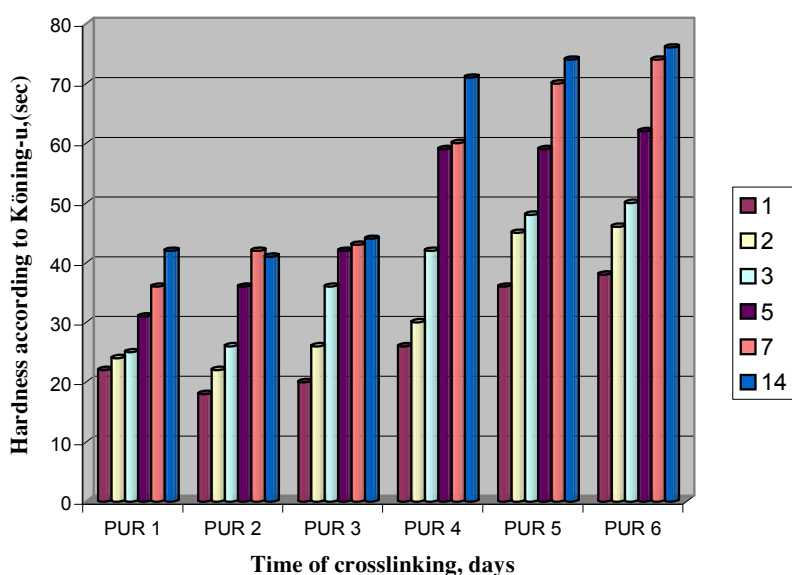


Fig. 2. The effect of hardness increase of two-component PUR compositions with polyols Luhydran LR 8833 and Luhydran LR 8845

The decrease of hardness according to König, that was examined in both systems (Fig. 3 and 4), with the growth of the induction time clearly points to a considerable value of the isocyanate reaction in the reaction vessel with the polyol and/or with water. The crosslinking reaction lacks the reacted components for film forming.

With the composition that includes the polyol Macrynal VSM 6299, the use of the zirconium catalyst made it possible to achieve according to König, two hours after the induction time, after seven days, a hardness of 181", while the application of the manganese catalyst enabled a hardness of 196" (Fig. 4).

The composition with the polyol Macrynal VSM 2521, (Fig. 5 and 6), also produced higher value of hardness upon seven days of drying, an induction time of two hours, with a more selective manganese catalyst of 216" relating to the zirconium catalyst of 205" (Fig. 6).

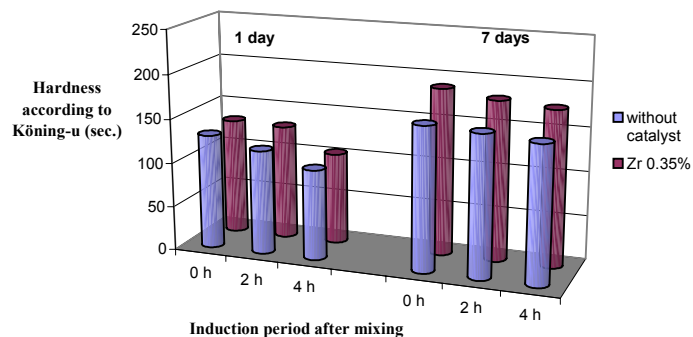


Fig. 3. The effect of the potlife on the coating hardness of the two-component PUR composition based on the polyol Macrynal VSM 6299 w/42 WA (PUR 7), without catalyst and with zirconium catalyst K-KAT® XC-6212 (dry film thickness 30 μm)

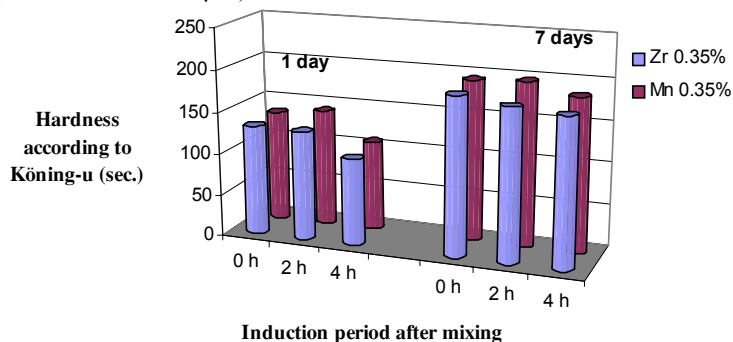


Fig. 4. The effect of the potlife on the coating hardness of the two-component PUR composition based on the polyol Macrynal VSM 6299 w/42 WA (PUR7), with the zirconium catalyst K-KAT® XC-6212 and with the manganese based catalyst (dry film thickness 30 μm).

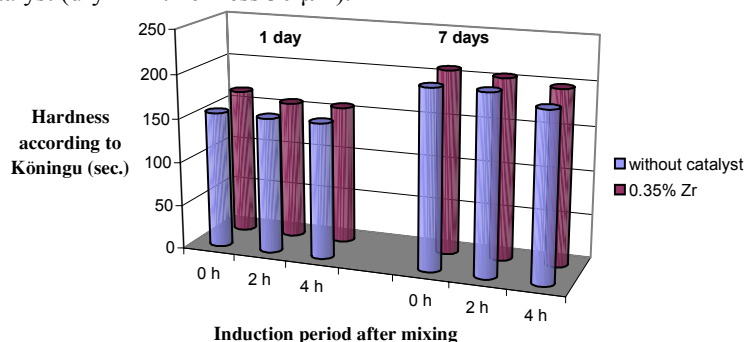


Fig. 5. The effect of the potlife on the hardness of the coating of the two-component PUR composition based on the polyol Macrynal VSM 2521 w/42 WAB (PUR 8), without the catalyst and with the zirconium catalyst K-KAT® XC-6212 (dry film thickness 30 μm)

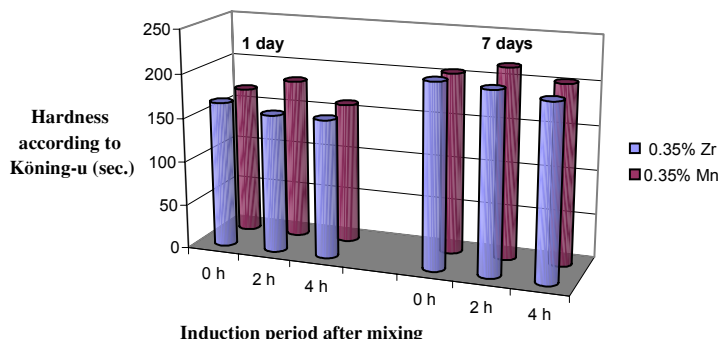


Fig. 6. The effect of the potlife on the hardness of the coating of the two-component PUR composition based on the polyol Macrynal VSM 2521 w/42 WAB (PUR 8), with the zirconium catalyst K-KAT[®] XC-6212 and with the manganese based catalyst (dry film thickness 30 μm)

According to the data obtained from literature, the reaction of water with the polyisocyanate component has the induction period of two hours and so the maximal effect of the activity of the catalyst is achieved just during that induction time [5].

Table 4. The measuring of gloss with the increase of the induction time in the composition with Macrynal 2521 (film thickness 30μm, film dried for 7 days at 295 K, angle 60°)

Time	Polyol 2521 Without catalyst	Polyol 2521 With K-KAT6212(0.35% Zr)	Polyol 2521 With complex (0.35% Mn)
0 h	115	116	116.8
2h	115	117	118
4h	114	116	117

Table 5. The measuring of gloss with the increase of the induction time in the composition with Macrynal 6299 (film thickness 30μm, film dried for 7 days at 295 K, angle 60°)

Time	Polyol 6299 Without catalyst	Poliol 6299 With K-KAT 6212(0.35% Zr)	Polyol 6299 With complex(0.35%Mn)
0 h	112	113	114
2h	111	113	115
4h	111	112	113

The catalytic effect also affects the gloss of the formed films (Tables 4 and 5). The maximal effect was achieved two hours after the induction time, which indicates that the most compact film with the minimal surface defects was formed.

CONCLUSION

The presented results show that the performances of the aqueous two-component polyurethane coatings depend on the polymer structure of the polyols and the polyisocyanates as well as on the selectivity of the employed catalyst.

The addition of the selective catalyst and favoring the isocyanate-polyol reaction contribute to obtaining a greater hardness of the formed films.

Concerning the catalytic activity, the results of the hardness tests show that the manganese complex obtains the highest catalytic activity two hours after induction time, which points to the optimal time of the catalyst effect.

The more selective catalyst enables us to obtain more optimal physical-mechanical properties of the aqueous two-component polyurethane coatings.

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ODREĐIVANJE NEKIH FIZIČKO-MEHANIČKIH KARAKTERISTIKA U VODENIM DVOKOMPONENTNIM LAKOVIMA PRIMENOM NEKALAJNIH KATALIZATORA

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Poslednjih godina upotreba vode umesto organskog rastvarača u premaznim sredstvima je znatno povećana. Ovo je posledica sve strožih zahteva za zaštitu životne sredine, kao i uspešnosti vodenih premaza u zaštiti materijala organskim prevlakama. Glavni aspekt u razvoju vodenih 2K-PU sistema je prvobitno naći metode za sprečavanje neželjene sekundane reakcije sa vodom i dobijanje najboljeg umrežavanja.

U ovom radu za umrežavanje od poliolskih komponenti korišćene su akrilne disperzije sa različitom vrednošću hidroksilnog broja. Kao umreživači korišćeni su vodoemulgujući poliizocijanati na bazi heksametilen diizocijanata sa različitim sadržajem NCO-grupa. Od katalizatora korišćen je komercijalni katalizator cirkonijuma (KAT[®]XC-6212) i manganov kompleks sa mešovitim ligandima na bazi derivata maleinske kiseline. Premazi su okarakterisani merenjem tvrdoće po Königu i sjaja po Lange-u korišćenjem katalizatora različite selektivnosti. U tom smislu praćen je i uticaj različitog indukcionog vremena posle mešanja komponenti na tvrdoću i sjaj formiranih filmova.

Dobijeni rezultati pokazuju da performanse vodenih 2K-PUR premaza zavise od polimerne strukture poliola i poliizocijanata kao i od selektivnosti primenjenog katalizatora.

Ključne reči: Vodeni premazi, umrežavanje, indukciono vreme, tvrdoća po König-u