

**CATALYSIS OF THE ISOCYANATE-HIDROXYL REACTION
BY NON-TIN CATALYSTS IN WATER BORNE
TWO COMPONENT POLYURETHANE COATINGS**

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Abstract. *Because of the high toxicity of some organotin compounds, there has been an attempt to ban organotin compounds from all coating applications. Organotin catalysts are not selective. They catalyze the reaction of isocyanates with hydroxyl groups from polyol and water and the hydrolysis of ester groups.*

One novel approach to control the water side reaction is the use of catalysts which selectively catalyze mentioned reaction.

In this paper, the impact of catalysts selectivity of Mn(III) complexes with mixed ligands, selective zirconium catalyst K-KAT 6212 and DBTDL on mechanical properties of water-borne two component polyurethane coatings was investigated, by using an FTIR method.

Much better performances can be achieved, using more selective catalyst. The performance is similar to those based on organic solvents, but with less content of volatile organic solvents (VOC).

Key Words: *Crosslinking, Waterborne Two Component Polyurethanes, Selective Catalyst, König Hardness*

INTRODUCTION

The catalysis of the isocyanate-hydroxyl reaction has been studied by many authors (1,2) who found that the reaction of aliphatic isocyanates with hydroxyl groups is catalyzed by many metal carboxylates and organic tin compounds.

In most coating applications side reaction with water is not desirable because it can lead to gassing and blister formation and also to poor cross-linking density. The water reaction of isocyanates is especially troublesome during cure under high humidity conditions or in two component water-borne isocyanate crosslinked coatings. The steric hindrance around the catalytic center was found to have strong effects on the rate constants for urethane reactions catalyzed by sulfonium catalysts. The reaction of isophorone diisocyanate with alcohols was studied in the absence and presence of dibutyltin dilaurate (DBTDL) and 1,4-diazabicyclo[2,2,2]-octane (DABCO). In the presence of DBTDL the reaction of the secondary isocyanate groups was favored, while in the presence of DABCO the reaction of the primary isocyanate group was preferred. Apparently the relative reactivity of the isocyanate group depends on the mode of catalysis and steric hindrance.

The relative selectivity (S), (equation 1) was measured as urethane IR peak area (P_{urethane})/ urea IR peak area (P_{urea}) ratio, by method Werner Blank (3):

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

After the integration of characteristic absorption max of urethane and urea was done, the relative selectivity was calculated.

FTIR identification of reactants and products is very important, because the urethane and urea are products of polyol and polyisocyanate reaction. It is also important because the elimination of side-reaction with water which gives undesirable urea and CO_2 is necessary. FTIR spectra of urethane, urea and urethane/urea mixture (1:1) are shown in Fig. 1

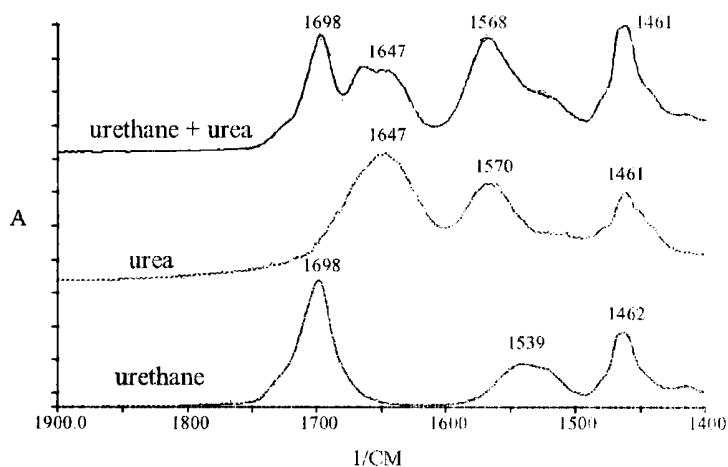


Fig. 1. FTIR spectra of urethane, urea and their mixture

A calibration curve of urethane/urea molar ratio vs. urethane/urea peak area ratio (Fig. 2) gave a good correlation with urethane to urea peak area ratio ranging from 0.5 to 3.5 (3),

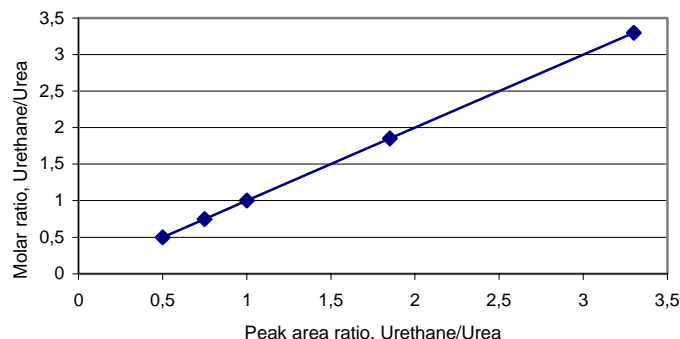


Fig. 2. Calibration curve of urethane/urea molar ratio versus IR peak area ratio

We were interested in finding alternatives to the catalysts that already exist and in developing compounds which exhibit increased selectivity for the isocyanate/hydroxyl reaction.

Comparing to the DBTDL catalyst, the complexes of Mn and Zr with acetylacetonates (acac), showed increased selectivity for the isocyanate/polyole reaction (4).

Considering all this, it was interesting to try and replace acac with other ligand and gained catalyst with increased selectivity for the isocyanate/hydroxyl reaction. This would also permit catalyst application in water-borne two component polyurethane formations.

The present paper describes the application of complexes with increased performance and their influence on physic-mechanical characteristics of water-borne two component polyurethane coatings.

EXPERIMENTAL

The compounds such as octoate of Zn, Co, Mn, as well as acac of Co, (King industries, Norwalk-USA). Butylisocyanate and 2-ethyl-1-hexanol (Merck-Schuchardt), were used as model compounds due to their similarity with aliphatic polyisocyanates and hydroxyl resins, as well as their relatively simple FTIR spectra. Mn-acac complexes with mixed ligands ((KML-1, KML-2, KLM-3) were prepared via original procedure (5).

The metal catalyst (previously dissolved in THF) and butyl isocyanate were added at the same time to stock solution of H₂O and 2-ethyl-1-hexanol. The solution was thoroughly shaken. The molar ratio of butyl isocyanate /alcohol/H₂O was maintained 1.0/1.0/2.0 for all the tests. The catalyst amount added was adjusted so that the isocyanate would be completely reacted in 5 hours under ambient temperature (ranging from 0.005 to 0.05 metal %). The uncatalyzed reaction took over 20 hours to complete under the same conditions.

Mn(III) acac complex with mixed ligands KLM-3 was dissolved in propylene glycol/methoxypropyl acetate in 9:1 ratio. The concentration of active Mn-substance was similar to concentration of Zr (0.38%) in K-KAT[®]XC-6212 (6). The percent of applied catalyst was calculated on the base of total hardness on applied system.

The polyol component used in this study as waterdispersion, commercially known as Luhydran[®] LR 8845, (BASF AG Germany) is a copolymer prepared via acrylic acid methacrylic ester and styrene, with solid content of 45%.

The polyol component (pH = 2) was stabilized using pH in range 5.5 - 7.5 by added triethanolamine. This is necessary to achieve optimal crosslinking and longer usage life.

Isocyanat reacts very slowly with water in the defined pH range. After that the coalescent was added to soften dispersion particles of polyole, to make easy the coagulation and to improve film formation. Coalescent are mainly ester alcohol solvents. We used ester alcoholate Texanol.

Since water systems usually make foam, it is necessary to use antifoamings in concentration 0.3-1%. The polyole composition is given in Table 1.

Table 1. The recepture of polyol component

Component A	Weight, %
Waterdispersion 8845 (45%)	175,49
Triethanolamine	1,8
Coalescent	14
Troykyd 999	1,2

The polyol component lived for 24 hours so it would have a better effect on global dispersion.

The polyisocyanat component used in this study is a hexamethylen diisocyanat derivate (HDI), commercially known as BASONAT[®]P LR 8878, (BASF AG Germany). This component is suitable for polymer dispersion containing OH-group. The isocyanat component is with NCO-group content of 17.5%.

After that, the polyol component is stirred with polyisocyanat component 10-15 min. Because of high viscosity, polyisocyanat was dissolved in methoxypropylacetate (50%). In the water system two component polyurethane coatings can be formulated in practice, containing organic solvents below 50 g dm⁻³ (50%).

After stabilization, the polyurethanic dispersions are made for investigation and application of films.

After the reaction was completed (disappearance of isocyanate checked by FT-IR in a sealed cell), a drop of the reaction solution was taken to make a thin film on a CaF₂ plate and the film was dried for 30 minutes under ambient temperature for each sample before recording the FT-IR spectrum. Bomem MB-100, Canada spectrometer was used for recording FT-IR spectrum. The urethane and urea peaks were integrated to calculate the relative selectivity (7).

The hardness and gloss of films were observed using catalysts with different selectivity. The hardness of lack films was determined via ISO 1522 method. The gloss was determined via Dr Lange's method in 60° angle (ISO 2813).

RESULTS

To choose the most selective catalyst, the model systems NCO/OH/H₂O = 1.0/1.0/2.0 with Zn, Co and Mn octoate, Co, Zn, Ni, Al and Mn acetylacetonate, Zr-catalysts K-KAT[®]XC-6212 and Mn complexes with mixed ligands (KLM-1, KLM-2, KLM-3), the analysis of FTIR spectra was necessary.

The variation of ligands, based on metal chelates, can change physic-chemical characteristics of chelates. It also can give complexes with different performance comparing to ligands themselves (8). This means synthesis and investigation of new catalysts. Considering this, we investigated Mn-complexes with mixed ligands in which the acac group is replaced with derivatives of maleic acid. These derivatives contain amino and sulpho-groups (complex KLM-1), tertiary amino and sulpho group (complex KLM-2) and hydroxomic derivative (complex KLM-3).

The most characteristic absorption mix was of investigated compounds isolated (Fig. 3). They show the different ratio of urethan/ urea preparation in system mentioned above, as well as adequacy of using of calibration curve.

The most characteristic spectra were selected indicating the different ratio of urethane/urea preparation in systems (Fig. 3) mentioned above.

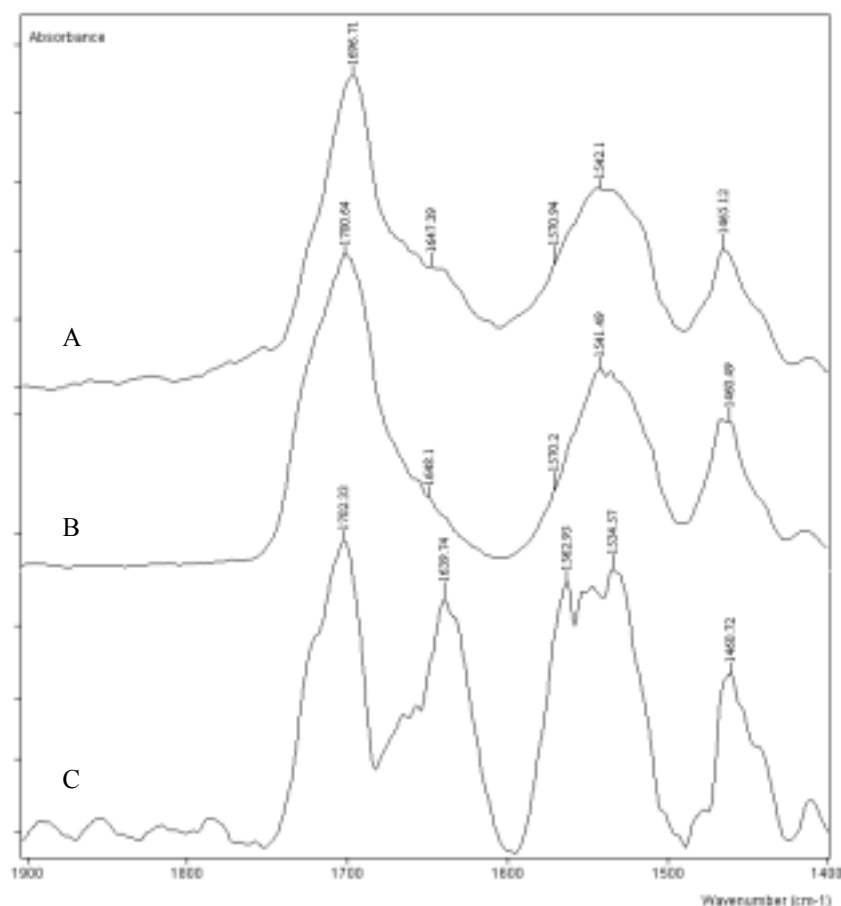


Fig. 3. Comparative FTIR spectra of catalyzed systems $\text{NCO}/\text{OH}/\text{H}_2\text{O} = 1,0/1,0/2,0$ with: A) catalyst of zirconium K-KAT[®]XC-6212 (King industries, Norwalk-USA); B) complex of Mn with acetylacetonate with mixed ligand KLM-3; C) Co octoat

FTIR spectra show that in range of $1650\text{--}1550\text{ cm}^{-1}$ (9), formation of is urea dominated for systems with Co-octoate catalyst. The absence of those vibrations and present of vibrations with absorption max. at 1400 cm^{-1} and 1540 cm^{-1} suggest formation of urethane in KLM-3 (Fig. 3b) and zirconium catalyst (Fig. 3a).

After the analysis of characteristic FTIR vibrations of all investigated compounds was done and their relative selectivity was calculated and the results are shown in Fig. 4.

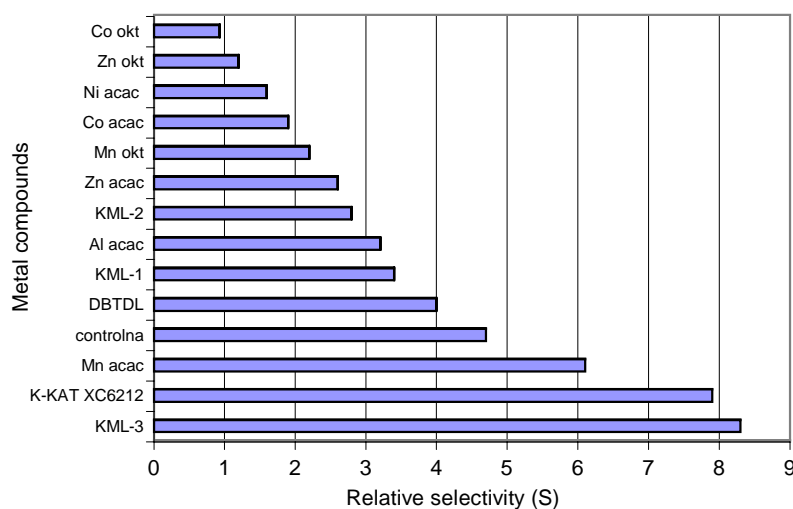


Fig. 4. Comparison of selectivity of different metal catalysts

The values of relative selectivity show that KLM-3 system possess best selectivity for isocyanat-hidroxy reaction ($S = 8.3$). Comparing the catalysts from the same group, it is shown that ligands in complexes are responsible for catalytic effect of investigated systems. Comparing the KLM-1 and non-catalyse systems the KLM-2 possess less selectivity (control probe, Figure 4), but they have better characteristics than octoate and acetoate. This suggests that an adequate ligand can effect the different selectivity which is higher in KLM-1 compound (10). KLM-3 compound has possibility for synergistic effect of Mn and amines in ligand. It is a very complicated mechanism and it would take more results to explain it.

The examination of some metal octoate and acetylacetonate selectivity shows that Mn-acetylacetonat possesses better catalyst selectivity comparing not only against octoate, but to other acetylacetonate (Zn, Co).

The results of measuring followed by dry and crosslinking process which can be observed by water evaporation from solvent and reactions of polyol/hydroxyl groups and hardness measured by König and gloss by Lange are given in Fig. 5, 6.

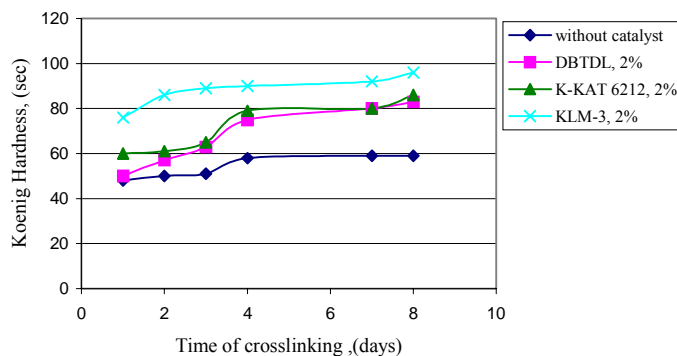


Fig. 5. The dependence of hardness change and time of crosslinking for dry films containing of : BASONAT[®]PLR 8878 0.6 g (50%_{r-r}, metoxypropyl acetate) + kom.A-7g(8845), film thickness 20 μ , in dependence of time, without catalyst and with catalyst of different selectivity

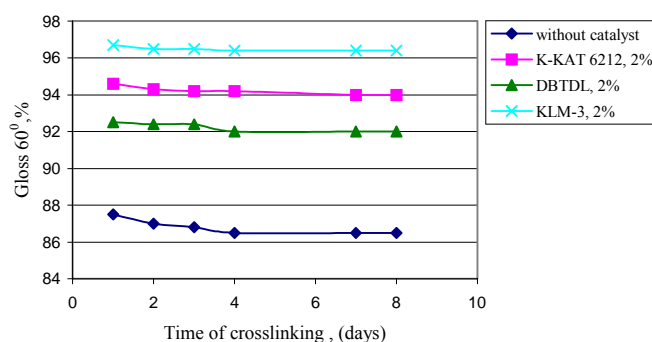


Fig. 5. The dependence of gloss change and time of crosslinking for dry films containing of : BASONAT[®]PLR 8878 0.6 g (50%_{r-r}, metoxypropyl acetate) + kom.A-7g(8845), film thickness 20 μ , in dependence of time, without catalyst and with catalyst of different selectivity

The results of process of crosslinking which were observed by hardness of dry films show that the reaction of isocyanate and polyole was favored using the more selective catalyst (KLM-3) in water-borne polyurethanic two component coatings. The degree of crosslinking and hardness is bigger (Fig. 5). The decrement of gloss is expected due to reaction of isocyanate components with moisture from atmosphere. When the more selective catalyst is used, the start values of hardness and measured gloss after period of observing crosslinking are bigger than when the commercial catalysts of tin and zirconium are used.

CONCLUSIONS

The integration of characteristic vibration for urethane formation in reaction system can be successfully used as a measure of relative catalyst selectivity in water-borne polyurethanic

two component coatings. The best selectivity in isocyanat/hydroxyl reaction ($S = 8.3$) is shown at Mn-complex with mixed ligands KLM-3. The investigation of certain metal octoate and acetylacetonate has shown that Mn-acetylacetonate possesses the greatest catalyst selectivity.

The more selective catalyst favors the reaction between isocyanat and polyol component. This increases the percentage of urethanic bonds and degree of hardness and of gloss in the formed films from two components waterborne polyurethane lacquers..

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SELEKTIVNA KATALIZA IZOCIJANAT-HIDROKSILNE REAKCIJE POMOĆU NEKALAJNIH KATALIZATORA U VODENIM DVOKOMPONENTNIM POLIURETANSKIM PREMAZIMA

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Zbog visoke toksičnosti u svetu postoji veliko interesovanje za zamenom organo kalajnih jedinjenja u premazima. Uz to, organokalajni katalizatori nisu selektivni. Oni katalizuju reakciju izocijanata sa hidrosilnim grupama i iz poliola i iz vode, kao i hidrolizu estarske grupe.

Nov pristup, bi bio u je korišćenju jedinjenja koja selektivno katalizuju navedene reakcije.

U radu je ispitivan uticaj selektivnosti katalizatora na bazi Mn(III)kompleksa sa mešovitim ligandima, selektivnog katalizatora cirkonijuma, K-KAT[®]XC-6212, kao i DBTDL, na mehaničke osobine vodenih dvokomponentnih poliuretanskih premaza, korišćenjem FTIR spektroskopije.

Izborom selektivnijeg katalizatora mogu se postići znatno bolje performanse, slične onima na bazi organskih rastvarača ali sa daleko manjim sadržajem isparljivih organskih rastvarača (VOC).