



UNIVERSITY OF NIŠ

The scientific journal FACTA UNIVERSITATIS

Series: Working and Living Environmental Protection Vol. 1, No 4, 1999, pp. 1 - 7

Editor of series: Ljiljana Rašković, e-mail: ral@junis.ni.ac.yu

Address: Univerzitetski trg 2, 18000 Niš, YU, Tel. +381 18 547-095, Fax: +381 18 547-950

<http://ni.ac.yu/Facta>

LATEST ACCOMPLISHMENTS IN WATERBORNE TWO-COMPONENT SYSTEMS FOR ORGANIC COATINGS

UDC 547

Ljiljana Rašković, Suzana Perošević

Faculty of Tehnology, Leskovac

Abstract. *Waterborne two-component systems are a manifestation of a technology of a later date, proven in a large number of applications. They show characteristics identical to those of two-component systems in organic solvents and at the same time they have an advantage to contain a reduced quantity of volatile organic solvents.*

The research, described in this paper was directed to waterborne two-component polyurethane systems formed with specially developed hydroxyl-functional dispersions and polyisocyanates that could emulgate with water. The paper discusses the chemistry of these systems in the light of their relevant importance for technical applications such as pot-life, froth and carbon dioxide development, film mechanical integrity development in order to achieve as good stability in hard operating conditions as possible.

INTRODUCTION

The use of waterborne coats for organic coatings has much increased over the past years. This is the consequence of the increasing environmental protection requirements and a successful application of waterborne coatings in the protection of materials for which organic coatings are used.

As waterborne coatings are accepted more and more and new technologies spring into life, research was directed to the development of waterborne coats suitable for hard ambient working conditions. Pursuant to that, research of waterborne two-component epoxy and polyurethane coatings supports the belief that waterborne coatings may withstand loads appearing in difficult working conditions.

Self-emulsifying epoxy resins [1] based on a mixture of bisphenols A and F are networked in a water solution with polyamidoamines, that also serve as emulsifiers.

The properties of the films formed from self-emulsifying epoxy resins and polyamidoamines from water solutions are very similar to the properties of the films

The main principle of the two-component polyurethane systems is high reactivity of an isocyanate group of polyfunctional isocyanates that reacts easily with hydroxyl groups of polyhydroxyl-functional oligomers or polymers while forming by cross connecting stable polyurethanes and structure [2].

Reactions with water are undesirable for two reasons:

Second, the carbon dioxide that appears may be captured in bubble form in dry film, produce an ugly appearance and unable cross connecting because of voids and holes in the dry film.

For this reason the research discussed in this paper was directed to waterborne two-component polyurethane formed with specially developed hydroxyl-functional dispersions and low viscose polyisocyanates or polyisocyanates that can emulsify with water [3], the objective being to get optimum physical and mechanical properties of the films and their satisfactory stability in exploitation.

Two polyfunctional dispersions with hydroxyl groups, copolymers from acrylic and metacrylic esters and styrene, pH values 2, OH number 100 and mean diameter of a 0.2 μm particle were used in the research namely:

Polyol PACD 8845 with the lowest temperature of film formation of 60 °C

and three kinds of water-emulsifying polyisocyanates on the basis of hexamethylene diisocyanates (HDI) namely:

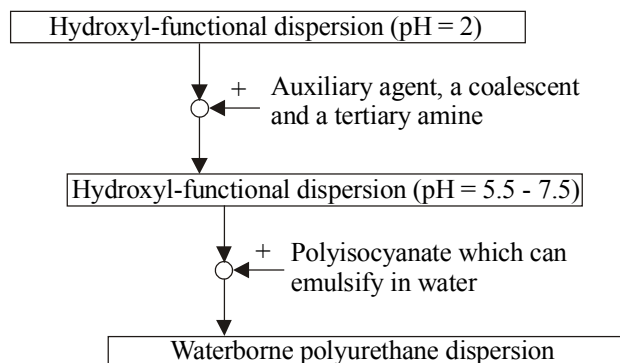
HDI-based polyisocyanate 8878 with an NCO group content of 17-18%

Modified HDI-based polyisocyanate 8901 with an NCO group content of 13.5–14.5% and HDI-based polyisocyanate 8963 with an NCO group content of 18.5–21.5%.

The following Table 1 shows the structure by weight of the formed polyurethane dispersions.

[illegible]

Waterborne polyurethane dispersions were prepared according to the following pattern:



Dry film adhesion degree, impact caused deformation and dry film hardness were done by the methods quoted in JUS standards.

The adhesion degree to the base was determined by cutting the film in form of a lattice using a special cutter. Such a formed lattice was inspected visually and its appearance was compared with the appearance of the lattice in the table for film adhesion degree classification.

Impact caused deformation, namely impact resistance of a film was measured indirectly by determining the height in cm from which a weight of 1 kg mass was dropped and did not cause any damage to the film.

The hardness of dry film was determined by an indirect way by measuring time in which amplitude oscillation was reduced by a pendulum lying on the film.

Table 2 shows adhesion degree and impact resistance of dry films to deformation.

Table 2. adhesion degree and impact resistance of dry films to deformation

Sample	Temperature (°C)	Networking time (min)	Adhesion degree JUS H.C.8.059	Impact resistance JUS H.C.8.060	Dry film thickness (µm)
PUD 1	80	30	0	100/90	50-60
	120	30	0	100/100	60-60
	140	30	0-1	100/100	65-68
PUD 2	80	30	0	100/100	50-93
	120	30	0	100/80	89-99
	140	30	0-1	80/75	80-84
PUD 3	80	30	0	50/20	52-75
	120	30	0	70/100	35-76
	140	30	0-1	100/70	79-99
PUD 4	80	30	0	100/100	49-105
	120	30	0	100/100	32-71
	140	30	0-1	90/100	32-69
PUD 2"	80	30	0	100/100	45-55
	120	30	0	100/70	32-45
	140	30	0-1	90/75	60-70
PUD 4"	80	30	0	80/52	26-57
	120	30	0	100/100	43-52
	140	30	0-1	100/50	50-70
PUD 5	80	30	0	100/100	31-57
	120	30	0	100/100	33-70
	140	30	0-1	100/100	52-68
PUD 6	80	30	0	100/100	27-71
	120	30	0	100/100	40-53
	140	30	0-1	100/100	70-72

Table 3 shows a change in dry film hardness when networked at different temperatures.

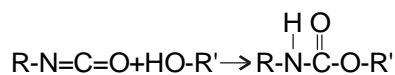
Table 3. Film hardness change at networking

Sample	Temperature (°C)	Networking time (min)	Hardness at JUS H.C.8.055 (sec Ko)	Dry film thickness (μm)
PUD 1	80	30	18	90
	120	30	21	70
	140	30	38	60-75
PUD 2	80	30	27	70-75
	120	30	29	72-90
	140	30	24	70-120
PUD 3	80	30	45	80-95
	120	30	48	72-78
	140	30	70	80-85
PUD 4	80	30	67	90-100
	120	30	98	70-100
	140	30	94	70-85
PUD 2"	80	30	42	70-90
	120	30	45	65-80
	140	30	63	40-53
PUD 4"	80	30	59	70-90
	120	30	78	62-72
	140	30	70	20-73
PUD 5	80	30	35	60-70
	120	30	43	40-60
	140	30	76	38-50
PUD 6	80	30	73	40-62
	120	30	119	42-50
	140	30	111	65-78

Since the best values of physical and mechanical properties at forced networking at increased temperatures were realized with the ratio of reactants in polyurethane dispersions PUD 5 and PUD 6, further tests were done by networking the films at the room temperature and were compared to the properties of polyurethane films in organic solvents, as shown on Table 4.

RESULTS AND DISCUSSION

With conventional two-component polyurethane systems based on organic solvents, the polyol component reacts with polyisocyanate, forming cross connected polymer according to the following reaction:



This reaction starts, as soon as the reactants – the two components are brought into contact. In such systems, viscosity is a relatively simple function of molecule mass and an increase in viscosity directly mirrors the measure at which the reaction progressed. The pot-life expiry (time of use) is normally demonstrated by significant increase in viscosity or gelling.

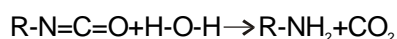
Table 4. Adhesion degree, impact resistance of dry film to deformation and change in the film hardness when networked at room temperature

Sample	Networking time (h)	Adhesion JUS H.C.8.059	Impact resistance JUS H.C.8.060	Hardness, JUS H.C.8.055 (sec Ko)	Dry film thickness (μm)
PUD 5	24	0-1	100/90	22	65-70
	96	0	100/90	24	65-70
	120	0	100/100	25	65-70
	168	0	100/100	31	65-70
	192	0	100/100	31	65-70
	240	0-1	100/80	36	65-70
	288	0-1	100/90	36	65-70
	312	0	100/100	41	65-70
	432	0	100/100	42	65-70
PUD6	24	0	100/100	36	65-70
	96	0	100/100	45	65-70
	120	0	100/100	48	65-70
	168	0	100/100	59	65-70
	192	0	100/100	63	65-70
	240	0	100/100	64	65-70
	288	0	100/100	70	65-70
	312	0	100/100	71	65-70
	432	0	100/100	74	65-70
PUR in organic solvents	24	0	100/100	18	60-65
	96	0	100/100	43	60-65
	120	0	100/100	45	60-65
	168	0	100/100	66	60-65
	192	0	100/100	71	60-65
	249	0	100/100	71	60-65
	288	0	100/100	72	60-65
	312	0	100/100	71	60-65
	432	0	100/100	78	60-65

When polyisocyanate and polyol dispersions are mixed before use, the reactions of isocyanate-hydroxyl group and the isocyanate–water will be initiated.

In literature (4,5,6,7) the reaction of polyisocyanate with a hydroxyl group is faster than its reaction with water.

However, a certain reaction with water is unavoidable [8] which is confirmed by the development of carbon dioxide in the following reaction:



The pot-life of waterborne two-component polyurethane systems is a more complex function and includes a large number of variables.

An increase in molecule mass due to polyol and polyisocyanate reaction in polymer stage need not bring about a noticeable change in viscosity in a continuous water phase.

However, the viscosity increase, which is in these systems often accompanied with abundant froth due to development of carbon dioxide defines the upper limit of pot–life (time of use).

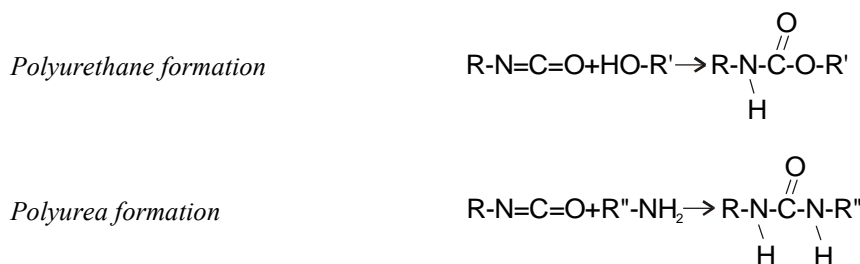
When the condition of polyurethane dispersion was visually monitored and viscosity determined by measuring liquid phase of samples by a JUS method for a period of 8 hours one may say that the applied formulation of reactants as well as the technology of

application gave very stable polyurethane dispersions.

This statement results from a slight change in viscosity in the course of a 8-hour long analysis. In this period a slight froth that appeared was noticed in PUD 1 and PUD 2 polyurethane dispersions after 4 hours. Generally it may be said that polyurethane dispersions with this composition of components prepared by the suggested technological procedure can be used in the period of 8 hours.

After applying polyurethane dispersions onto bases easily volatile materials (water and solvent) started evaporating. The major portion of water evaporated in the course of 60 min. This compacted the particles and enabled better diffusion and reaction.

At the end a film of cross connected polymers was formed



Development of mechanical properties, which was monitored by assessing adhesion, hardness and impact resistance to deformation by forced networking and networking at room temperature. The results show that the adhesion at the dry base occurs quickly which is confirmed by acceptable performances 24 hours after application.

The hardness of the coating developed somewhat at a slower pace in the course of the first three days and then increased to the maximum of about 18 days.

The obtained values for mechanical properties of the films of polyurethane dispersion PUD 6 were equal to the mechanical properties of the films of polyurethane with organic solvents – Table 4. These results correlate well with the results of IR spectroscopy – tests are in progress.

CONCLUSIONS

After the application, evaporation of easily volatile substances occurred in the course of 60 min.

After this period the particles came into contact in the whole film. When this happened the diffusion of molecules along molecule surfaces led to particle coalescence. This contributes to the reaction of isocyanate/hydroxyl group. Three days later, mechanical integrity of the film pointed to significant cross connection. The quantity of polyisocyanate in the formulation of polyurethane dispersion reactants allowed a full hydroxylic reaction of isocyanate-water.

These tests of the formation of two component films of polyurethane systems allow us to form a framework for further studies and better understanding of the technology of waterborne two component polyurethane systems that are considered prospective for environmental protection and for the surfaces of protective coatings.

REFERENCES

1. Ciba Geigy. Wasserverdunnbares, kalthardetes Epohydharz – sistem auf Basis von Arasdit Py 340-2/HZ 340, Publ. No. 24852/2/d Schweiz (1996)
2. Lj. Raskovic. Osnova polimernog inženjerstva /Basis of Polymer Engineering/, Faculty of Technology Leskovac, Leskovac, (1995)
3. D.I. Fischer. Aqueous 2-Pack-PUR-Systems based on OH-functional Dispersions and Polyisocyanates, Technical Seminar II, BASF AG, Ludwigshaven (1997)
4. P.B. Jacobs, P.C. Yu. Two-Component Waterborne Polyurethane Coatings, Journal of Coatings Technology, 65, No. 822 (1993) 45
5. C.H. Hare. Protective Coatings: Fundamentals of Chemistry and Composition, Technology Publishing Co., Pittsburgh P.A. p. 263
6. S.D. Senecker, T.A.Potter. Solvent and Catalyst Effects in the Reaction of Dicyclohexyl-methane Diisocyanate with Alcohols and Water, Journal of Coatings Technology, 63, No. 793 (1991) 19
7. D. Ihms, J.O. Stoffer, D.F. Schneider and C.Clain. The Effect of Catalysts on Kinetics and Mechanism of Urethane Film Formation, Proc.10th Waterborne High – Solids and Powder Coatings Symposium, New Orleans, L.A., February, (1983) 16-18
8. F.L. Brown, J. Polymer Sci., 22 (1956)423

NOVIJA DOSTIGNUĆA U VODENIM DVOKOMPONENTNIM SISTEMIMA ZA ORGANSKE PREVLAKE

Ljiljana Rašković, Suzana Perošević

Vodeni dvokomponentni sistemi predstavljaju noviju tehnologiju, koja se dokazuje u velikom broju primena. Oni pokazuju karakteristike podjednake kao i dvokomponentni sistemi u organskim rastvaračima, a u isto vreme imaju tu prednost da sadrže smanjenu količinu isparljivih organskih rastvarača.

Istraživanja u ovom radu usmerena su na vodene dvokomponentne poliuretanske sisteme, formirane sa specijalno razvijenim hidroksifunkcionalnim disperzijama i poliizocijanatima, koji mogu da se emulguju vodom. Ovde se govori o hemiji ovih sistema u svetlu njihove relevantnosti prema tehničkoj primeni na pr. pot-life, razvoj mehaničkog integriteta filma sa ciljem postizanja što veće postojanosti u teškim uslovima eksploatacije.