**Epoxy Waterborne Compositions Modified by Hydroxyurethanes**

*Oleg Figovsky1, Olga Birukova2, Alexander Leykin2, Leonid Shapovalov2*

*1Hybrid Coating Technologies, Inc., Daly City, CA, USA*

*2Polymate Ltd. – International Nanotechnology Research Center, MigdalHaEmek, Israel*

[*figovsky@gmail.com*](mailto:figovsky@gmail.com)

**Abstract:** Compositions of receiving and using waterborne epoxy - NIPU coating were developed. Experiments to study the compatibility of components in the waterborne epoxy - NIPU coatings were carried out. The optimum ratio of the components of the composition, in order to obtain the necessary physical and mechanical properties of the coating was determinate. The optimal compositions were recommended for industrial application.

**Key worlds:** coating, epoxy & nonisocyanate polyurethane, waterborne system, physical and mechanical properties.

Although the technology of water borne has been around formany years, great advances have occurred in the last decade [1-3].

Gone are the days where additive suppliers had little or any knowledgeof waterborne epoxy systems. Today, the combination of high-performance waterborne resins and hardeners, with fit-for-purposeadditives and co-solvents, gives formulators the opportunity to get thehighest performance you can expect from epoxy and still adhere to environmental regulations at the same total cost. Regulatory initiatives to meet clean air standards continue to be the main impetus for coating formulators to consider waterborne epoxy systems. This aggressive regulatory environment is nothing new and hasbeen the case for over 20 years, since the passing of the Clean Air Actin 1990. Today, the US Environmental Protection Agency (EPA),

Ozone Transport Commission (OTC), California Air Resources Board (CARB) and South Coast Air Quality Management District (SCAQMD) continue to set more and more restrictive limits on the Volatile Organic Compound (VOC) content in architectural and industrial maintenance

(AIM) coatings. However, there is a change in the air again. Asset owners and architects are now exercising new drivers for change, creating a high demand for green and sustainable products that canbe certified. No longer is it just a legislative requirement that is pushingfor change, but consumer demand. The benefits of waterborne epoxysystems versus conventional epoxy systems are now quite often thedeciding factor in coating selection by decision makers. For example, we have found many cases where the following benefits have been thekey factors in favor of waterborne epoxy systems:

• Ultra low VOC

• Very low odor

• Non-flammable/non-combustible

• Fast dry and re-coat

• Ease of cleanup (no solvents needed)

• Balanced overall performance properties

If these types of benefits can be obtained at an equivalent or slightlyincreased cost, owners and contractors will always choose waterbornesystems. The key aspect for proper performance and ultimately, usersatisfaction, is the proper selection of epoxy resin and curing agent forthe targeted application and substrate.

Water borne Epoxy (WBE) compositions are an unique set of products that enable the compiler to produce liquid curable materials with required viscosity, without the use of volatile organic compounds (VOCs).

This article describes the work in developing amines cure WBE compositions, which contain hydroxy-urethane modifier (HUM) [4-10].

Novel hydroxyurethane modifiers (HUM) for "cold" cure epoxy composite materials were synthesized. Properties of modified epoxy materials were studied by physical-mechanical and physical-chemical methods. It is established that the compositions with HUM demonstrate a significant increase in speed of curing process, as well as non-trivial increase in abrasion resistance and a marked improvement in strength properties. Other characteristics, such as chemical resistance, are not worse. General concept of generating new multifunctional modifiers was created. The HUM, which possesses a wide range of hydrogen bonds, embedded in epoxy polymer network without a direct chemical interaction [4].

We studied the influence of the nature and content of the HUM on the properties of materials. Enrichment of different polymer dispersions werealso investigated.

New modified compositions can be used in most conventional applications, such as coatings, floorings, adhesives, etc. without sacrificing performance.

Known waterborne epoxy composition consisting of water-base dispersions containing an epoxy resin, pigments, surfactants, other additives and aqueous emulsion of hardener. The use of water-based epoxy compositions instead of epoxy coatings withsolvents eliminates the loss of large amounts of solvents. Such compositions are less toxic and fire- and explosive proof in use.

These compositions have a high viability, coatings characterized by good physical, mechanical and barrier properties, and they are widely used in many industries.

Hexion's EPI-REZ™ Epoxy Waterborne Resins and EPIKURE™ Curing Agents for waterborne systems are an unique portfolio of products that are compatible with each other, and allow the formulator to develop waterborne formulations that in many instances are capable substitutes to formulations containing a high portion of Volatile Organic Compounds [2].

These combinations can generally be diluted to a desired solids level simply with water addition. Due to their high degree of compatibility with many components, EPI-REZ Waterborne Resins and/or EPIKURE Curing Agents can also be formulated with wetting agents, additives, cosolvents and coupling agents to obtain formulations for fast dry as well as high after cure corrosion resistance and superior adhesion to various substrates.

However, water-based epoxy compositions’ resistance to impact, bending and abrasion is low, which reduces the coating durability.

OBJECTS AND METHODS

The following raw materials were used:

-epoxy resin DER 324 (standard diglycidyl ether of bisphenol A,( Dow Chemical, USA )

-cycloate A ( aliphatic tricyclocarbonate, (Polymate Ltd, Israel )

-propylene carbonate( Huntsman, USA )

-ancamine 2280 ([Air Products](http://www.airproducts.com/products/product-finder/product-list/ancamine-teta.aspx?itemId=45D15B1D1ECD4EBABB3DA39160AF2F23&itemType=tn), USA )

- ancamine 2608 ([Air Products](http://www.airproducts.com/products/product-finder/product-list/ancamine-teta.aspx?itemId=45D15B1D1ECD4EBABB3DA39160AF2F23&itemType=tn), USA )

- ancamine K- 54 ([Air Products](http://www.airproducts.com/products/product-finder/product-list/ancamine-teta.aspx?itemId=45D15B1D1ECD4EBABB3DA39160AF2F23&itemType=tn), USA )

-Ti-pure R-706 (pigment, Chemours, USA )

-Hum (hydroxyurethane modifier (Polymate Ltd, Israel)

-Nephelinesyeniteminex 4 (filler,Uniminorporation, USA )

-Disperbyk 194/019 ([Wetting and dispersing additives](http://www.byk.com/en/additives/additives-by-name/disperbyk.html), BYK Inc USA)

-WB Hardeners DEH 800,804,805,810,813 (Dow Chemical, USA )

Testing were carry out by the following standards:

-Hardness (Shore D) ( ASTM D2240 )

Tensile strength, MPa( ASTM D638 M )

-Elongation at Break % (ASTM D638 M)

-Wear resistance, mg (ASTM D4060 )

The aim of our work was to increase the resistance of the WBE coating to abrasion, bending and impact, as well as to increasecoating elasticity, the possibility of applying it on the fresh concrete.

To achieve this target we tested the options of inclusion in HNIPU aqueous dispersion compositionhydroxy-urethane modifiers (HUM), which allowpreserving the advantages of epoxy coatings, and acquiring the useful properties of urethanes.

Considering the possibility of introducing HUM in WBE composition HUM, we concluded that in this case it is not possible to add a modifier in an aqueous dispersion part - whether it is an epoxy part or amine part, since under the influence of the water, modifier hydrolyzes and loses its advantages. Therefore, the shelf life of such formulations will be short. From this aspect, the decision was to add HUM in partwhich does not contain water, whether it is amine or epoxy part.

Thus, the following compositions were developed:

Option 1: A simple addition of water to an existing composition HNIPU.

Table 1

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No | PART A base | | | PART B hardener | | | | PROPERTIES | | | | | |
|  | DER-324 | Cycloate A | PС | Anc.2280 | Anc. 2608 | Anc. K-54 | % Water | Pot Life min | Appearance | Tensilestrength MPa | Elongation % | Hardness Shore D | Wear, mg |
| 3824 | 55 | 5 | 2 | 22 | 12 | 4 | 0 | 90 | gloss | 30 | 9 | 74 | 25 |
| 3842 | 55 | 5 | 2 | 22 | 12 | 4 | 5 | 80 | gloss | 30 | 12 | 72 | 25 |
| 3842 | 55 | 5 | 2 | 22 | 12 | 4 | 10% | 60 | gloss | 20 | 8 | 67 | 27 |
| 3842 | 55 | 5 | 2 | 22 | 12 | 4 | 20% | 30 | semi-gloss | 25 | 5 | 70 | 28 |
| 3842 | 55 | 5 | 2 | 22 | 12 | 4 | 30% | 20 | sticky | - | - | - | - |

Experimental results show that the optimum addition of water into existing HNIPU composition is 10-20%. It has practically no effect on the physic or chemical properties of the coating, accelerates the curing time and allows reducing the viscosity of the system without the use of organic solvents.

Option 2

A composition where PART A containsEPOXY RESIN and HUM, and PART B - hardener that contains aqueous emulsion of the amine with adduct.

After a number of tests, the optimal ratio of the components was selected for these compositions. See tables 2, 3.

 Table 2 shows the HNIPU water-dispersed compositionwith addition of HUM - 10% of epoxy resin content:

Table 2

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | PARTAbase | | PARTBhardener | | | | | |
| No. of  sample | EPOXY RESIN DER-324 | HUM | Ti-Pure  R-706 PIGMENT | NephelineSyenite Minex 4 FILLER | DISPER-BYK  194/BYK-019 | WB-HARDENER | Water | Viscosity Part A, Part B CPs |
| 7583 | 25 | 2.5 | 10 | 15 | 6/1 | DEH 804 | 18 | B=1080  A=240,  A+B= 1200 |
| 7584 | 25 | 2.5 | 10 | 15 | 6/1 | DEH 810 | 25 | B=1080,  A= 540,  A+B= 1270 |
| 7585 | 25 | 2.5 | 10 | 15 | 6/1 | DEH 800 | 30 | B=1080,  A=1240  A+B= 1800 |
| 7586 | 25 | 2.5 | 10 | 15 | 6/1 | DEH 805 | 30 | B=1080, A=1000 A+B= 2350 |
| 7587 | 25 | 2.5 | 10 | 15 | 6/1 | DEH 813 | 25 | B=1080,  A= 1700  A+B= 2350 |

The experimental results of option 2:

Table 3

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| No  sample | PotLife | Appearance | Tensilestrength MPa | Elongation, % | Pencil Hardness | Wearresistance |
| 7583 | 1h | matt | 12,5 | 4,6 | 2H | 52 |
| 7584 | 1,5h | glossy | 22 | 8 | 2H | 108 |
| 7585 | 1,5h | semi-gloss | 20 | 18 | 2H | 88 |
| 7586 | 40 min | matt | 23 | 12,5 | 2H | 78 |
| 7587 | 40 min | semi-gloss | 17 | 16,7 | 2H | 84 |

Fig.1

**Conclusions**

Compositions of receiving and using waterborne epoxy-urethane coating were developed.Experiments to study the compatibility of components in the waterborne epoxy-urethane coatings were performed.The optimum ratio of the components of the composition, in order to obtain the necessary physical and mechanical properties of the coating wasdeterminate.The laboratory batch tests of waterborne epoxy-urethane coatings, by applying the compositions to wet concrete samples were provided.The positive results were obtained.

**References**

1. Huntsman Waterborne Epoxy Systems for Coatings. Selector Guide.http://www.huntsman.com/advanced\_materials/Media%20Library/global/files/US%20Waterborne%20Systems%20Selector%20Guide.pdf.
2. Hexion Epoxy Waterborne Resins & Curing Agents http://www.hexion.com/epoxywaterborne.
3. Cook Michael Formulating novel aqueous epoxy resin systems for metal primer applications http://www.halox.com/formulations/files/Waterborne%20Epoxy% 20Primer%20based%20on%20SW-111.pdf.
4. Figovsky Oleg, Leykin Alexander, Shapovalov Leonid, NON-ISOCYANATE POLYURE-THANES – YESTERDAY, TODAY AND TOMORROW ENVIRONMENTALLY CONSCIOUSFACTORIES 2016, ICJ, AEE, pp. 95-108.
5. Birukova Olga, at all Pat US 2010/0249337 A1, 2010.
6. Figovsky O., Baranov O., Leykin A., Shapovalov L. Hybrid epoxy-amine hydroxyurethane-grafted polymer. Inženernyj vestnik Dona (Rus), 2009, №1 URL: ivdon.ru/ru/magazine/archive/n2y2016/3625.
7. Figovsky O., Beilin D., Leykin A. Nanostructured Composites Based on Interpenetrated Polymer Networks Nonisocyanate Polyurethanes Based on Cyclic Carbonates and Nanostructured Composites Part I. Inženernyj vestnik Dona (Rus), 2009, №1 URL:ivdon.ru/ru/magazine/archive/n2p2y2015/3131.
8. Figovsky O., Beilin D., Leykin A.  Nanostructured Composites Based on Interpenetrated Polymer Networks Nonisocyanate Polyurethanes Based on Cyclic Carbonates and Nanostructured Composites Part II. Inženernyj vestnik Dona (Rus), 2009, №1 URL: ivdon.ru/ru/magazine/archive/n3y2015/3132.
9. Figovsky O.,  Beilin D. Nanostructured Composites Based on Interpenetrated Polymer Networks Kinds, Classification, Properties, Synthesis, Application. Inženernyj vestnik Dona (Rus), 2009, №1 URL:ivdon.ru/ru/magazine/archive/n3y2015/3113.
10. Figovsky O., Cornille A., Auvergne R., Boutevin B., Caillol S. Environment friendly Polyurethanes: Nonisocyanate Synthesis. Zhurnal "Al'ternativnaya energetika i ekologiya" (Rus), №23-24, 2016, pp. 52-87.