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P90: EFFECTS OF BIOCIDAL REGULATIONS ON POLYMER PRODUCERS

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ABSTRACT: Biocide actives can be hazardous for both human health and environment so their amount of usage is limited by particular regulations. Recently second revision of EC 1272/2008 GHS, also known as CLP regulation in European Union is announced. The usage limits of biocide actives which may cause allergic reactions, have been lowered with the revision in EUH 208 statement. Organik Kimya has different business units; which produce emulsion polymerization products for Pressure Sensitive Adhesives & Paper, Coating, Industrial Adhesive, Textile & Leather Performance, Life Sciences & Material, Construction solutions. EUH 208 regulation is more important for the paint producers. They are producing the consumer products with formulations which highly include polymer binder. Organik Kimya follows closely the new regulations regarding protection of human health and environment, and leads the studies for EUH 208 in Turkey. 5 different biocide packages and 17 different products are handled and according to customer requests, 2 products adequate for EUH 208 regulation and 3 MIT- free products have been commercialized in coating solutions.

Keywords: EUH 208, MIT, BIT, CMIT/MIT, Polymer

INTRODUCTION

In the dynamic chemicals market, Organik Kimya is up to the task of meeting the demands of the various markets with Istanbul and Rotterdam plants, and state of the art R&D Center. With an annual capacity of 250.000 metric tons, supplying more than 1000 customers in over 85 countries Organik Kimya has become one of the major players in the market. The product portfolio of Organik Kimya includes more than 150 types of polymer emulsions, regular and tailor made products as well as new Innovative Solutions that provide value for a wide variety of applications for Coating, Construction, Industrial Adhesives, Life Sciences and Material, Pressure Sensitive Adhesives & Paper and Textile & Leather Performance Solutions.

The purpose of using in-can preservatives in the emulsion polymerization system, is to minimize the bacterial contamination risk during the shelf-life of the product. Biocidal actives can be hazardous for both human health and environment, so their amount of usage is limited by particular regulations.

Recently second amendment of EC 1272/2008 GHS, also known as CLP regulation in European Union is announced. The usage limits of biocidal actives which may cause allergic reactions, had been lowered with the revision in EUH 208 statement.

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Table 1. Concentration limits for biocide actives

Active	Skin sensitizer, H317, specific concentration limit	Concentration limit for the statement since 31th May 1999	Concentration limit for EUH 208 from 1th June 2015
BIT	≥ 500 ppm		≥ 50 ppm
CIT/MIT	≥ 15 ppm		≥ 1.5 ppm
DCOIT	≥ 300 ppm		≥ 30 ppm
MIT	≥ 1000 ppm	≥ 1000 ppm	≥ 100 ppm
OIT	≥ 500 ppm		≥ 50 ppm
EDDM	≥ 10000 ppm	≥ 1000 ppm	≥ 1000 ppm
TMAD	≥ 320000 ppm	≥ 1000 ppm	≥ 1000 ppm
PHMB	≥ 10000 ppm	≥ 1000 ppm	≥ 1000 ppm
IPBC	≥ 10000 ppm	≥ 1000 ppm	≥ 1000 ppm
DBNPA	≥ 10000 ppm	≥ 1000 ppm	≥ 1000 ppm
Glutaraldehyde	≥ 5000 ppm	≥ 1000 ppm	≥ 1000 ppm
Terbutryn	≥ 30000 ppm	≥ 1000 ppm	≥ 1000 ppm

I. LITERATURE ON BIOCIDES

Isathiazolone biocides have proven efficacy and performance for microbial control in a variety of industrial water treatment applications. Isothiazolones utilize a two-step mechanism involving rapid inhibition of grawth and metabilism, followed by ireversible cell damage resulting in loss of viability.

The most frequently use product is a 3:1 ratio of 5- cloro-32-methyl-4-isothiazolin-3-one (CIT) and 2- methyl-4-isothiazolin-3-one (MIT). CIT/MIT has broad spectrum efficacy versus bacteria, algae, and fungi. 1,2-benzisothiazolin-3-one (BIT) prodcuts have been used in a limited reange of industrial applications requiring long term preservation for bacterial control.

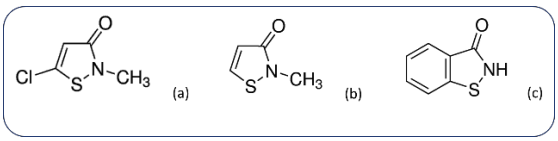

Figure 1. Molecular Structures of Isothiazolinones, (a) CIT, (b) MIT, (c) BIT

Limiting concentrations of isothiazolones resulted in search of new complementary molecules that exibit antibacterial and antifungal properties. One of the preffered biocide active, which is widely used as cosmetic preservatives and general antimicrobial agents is Zinc Pyrithione (ZnPT). It is known known to be active against fungal cell walls, associated membranes and bacterial transport processes.

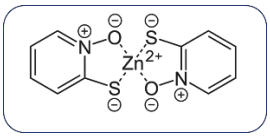

Figure 2. Molecular Structure of ZnPT Polymer dispersions for the most part are aqueous-based formulations. The polymer dispersion is used in a wide variety of applications. The composition of polymer dispersions with high water content and high nutrient level provides an environment that is perfect for the proliferation of microbial growth.

In polymer dispersions residual monomers inhibit microbial growth. Due to the toxicity of monomers, producers tend to lower the residual amounts, which causes the products to be more susceptible to contamination. The pH of the polymer emulsion also effects the microbial growth. Products with low pH values are rarely prone to bacterial contamination. However, as the pH of the product increases, the product becomes more susceptible. The biocide used must not only be stable but must be active over the pH range of the product. Residual inorganic redox agents can affect the stability of biocides by reducing the activity in aqueous phase.

Table 2. Effect of redox potential on stability of Isothiazolones

Redox Potential	Stability of CIT/MIT	Stability of BIT
>+100 mV	good	unstable
+50 mV to +100 mV	moderate	very poor
0 to +50 mV	poor	poor
0 to -50 mV	unstable	moderate
<-50 mV	very unstable	very good

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EXPERIMENTAL WORK & RESULTS

Organik Kimya follows closely the new regulations regarding protection of human health and environment, and leads the studies for EUH 208 in Turkey. Organik Kimya uses mainly combinations of different isothiazolinones (MIT, BIT, CMIT&MIT) for in can preservation. Depending on the amount, labelling with EUH 208 statement ('Contains (MIT/BIT/CIT-MIT). May produce an allergic reaction') is required.

EUH 208 regulation is more important for the paint producers. They are producing the consumer products with formulations which contain high amount of polymer.

For EUH 208 regulation, MIT + BIT + Znp package and for MIT Free BIT+ 2,2-dibromo-3- nitrilopropionamide (DBNPA) package used in our products. Color change and viscosity problem were observed in some cases.

Table 3. Experimental work on EUH 208 and MIT Free versions of Organik Kimya products

	POLYMERS	BIOCIDE PACKAGE	RESULTS
EUH 208	Styrene acrylic copolymers	50 ppm BIT + 100 ppm MIT + 50 ppm ZnP	At low Tg values, the package did not protect. At high Tg values, the package protected but color change (pink) and viscosity problem were observed due to ZnP in some cases.
	Vinyl acrylic copolymers	50 ppm BIT + 100 ppm MIT + 50 ppm ZnP	The package protected our products but color change (grey) was observed due to ZnP in some cases.
	Acrylic polymers	50 ppm BIT + 100 ppm MIT + 50 ppm ZnP	The package protected our products.
MIT FREE	Styrene acrylic copolymers	450 ppm BIT & 90 ppm DBNPA	According to redox potential, the package protected our products. At high redox potential, BIT was not stable.
	Vinyl acrylic copolymers	450 ppm BIT & 90 ppm DBNPA	The package protected our products.
	Acrylic polymers	450 ppm BIT & 90 ppm DBNPA	According to redox potential, the package protected our products. At high redox potential, BIT was not stable.

CONCLUSION

Optimum biocide packages have been determined which complies EUH 208 regulation and MIT Free products developments by using different biocides from various suppliers for acrylic and styrene acrylic polymers. In this study, 5 different biocide packages and 17 different products are handled and according to customer requests, 2 products adequate for EUH 208 regulation and 3 MIT-free products have been commercialized in coating solutions. The studies are ongiong for different products.

REFERENCES

Williams, T.M., (2007). The Mechanism of Action of Isothiazolone Bicoides. Power Plant Chemistry, 9(1), 14-22.

Gillat, J., (1997). The Effect of Redox Chemistry on the Efficacy of Biocides in Polymer Emulsions. Surface Coatings International, (4), 172-177.

Dinning, A.J., et. all, (1998). Pyrithione biocides as inhibitors of bacterial ATP synthesis. Journal of Applied Microbiology, (85), 141–14