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PRODUCTS OF ISOBUTYL ALDEHYDE CONDENSATION AS ECOLOGICAL SOLVENTS AND COALESCENTS IN PAINTS AND VARNISHES

The great variety of existing chemically diversified volatile organic compounds and coalescents are being replaced by so-called „green" solvents or high-boiling liquids of natural origin. The requirement to reduce the emissions of volatile organic compounds (VOC's) is imposed by the laws of the European Union and addressed, first of all, to the manufacturers of paints and varnishes. The level of VOC's in paints may be reduced by various methods, e.g., by developing paint formulations that contain coalescents and solvents other than those classified as VOC's. A method to achieve the above objective is to replace alkyl ethers (classified as VOC's) that are commonly used in water-based paint and varnish formulations, with hydroxyester HE-1, which is not prohibited. The concept for development of production of the hydroxyester HE-1 in Poland is based on the possibility of management of the existing raw material base and technological facilities of the Oxo Plant in the "Kędzierzyn" Nitrogen Works, Kędzierzyn-Koźle. The product is safe in use, not classified as VOC, and shows no toxicological or ecotoxicological properties.

1. Introduction

Solvents are predominantly used for making protective coatings. From the point of view of chemistry, there are a wide range of such coatings, including liquid hydrocarbons and chloroorganic derivatives, which are a serious burden to the natural environment due to their physical and chemical properties. Such solvents are being regularly replaced by new generation products, which are more environmentally friendly. The tendency is based on the EU legislation, intended to reduce the emissions of volatile organic compounds (VOC's), including a new regulation in the matter of registration, evaluation and authorization of chemicals in the light of the requirements of REACH.

Consequently, it is expected that major restructuring processes will be required in the solvent manufacturing industry, resulting from changes in the

structure of their consumption in the paint and varnish industry, which is the key industry for the solvents market, and from other factors.

Starting from the 1st of January 2007, the so-called "Decopaint Directive" (European Directive 2004/42/EC) came into force [3]. The Directive relates to reduction of the emissions of solvents from decorative paints and automotive varnishes which were not covered in the previous directive (1999/13/EC), limiting solvent emissions. Restrictions of the levels of VOC's were imposed in the directive and they are implemented in two steps: in the year 2007 and in the year 2010 (Fig. 1 and Fig. 2).

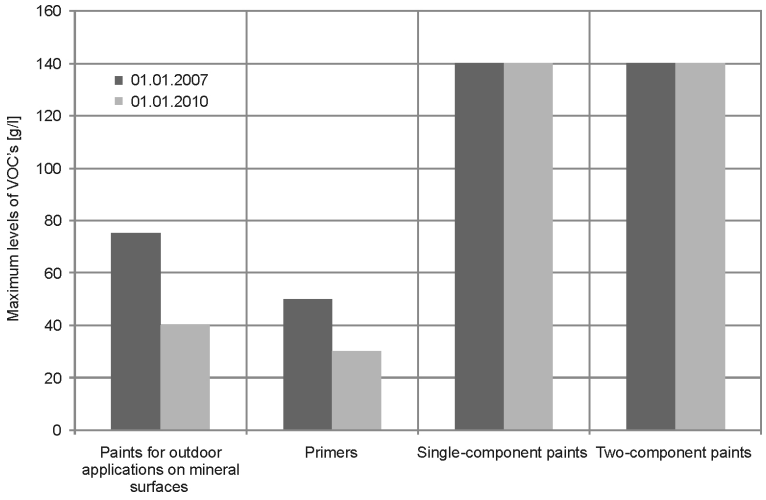


Fig. 1. Maximum levels of VOC's in water-based paint formulations

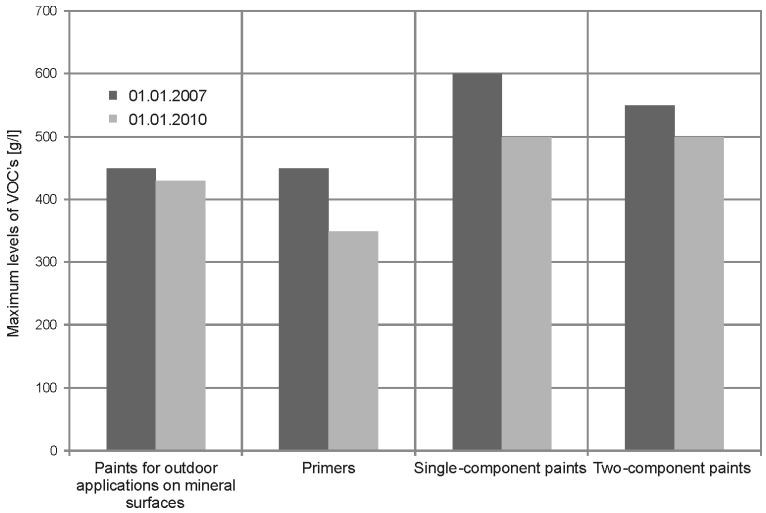


Fig. 2. Maximum levels of VOC's in solvent-based paint formulations

According to the Directive 2004/42/EC, every substance that has an initial boiling point at a temperature of 250°C or lower, as measured at 101.3 kPa, is classified as a Volatile Organic Compound (VOC).

The environmental burden on the part of VOC's results from the fact that they tend to react with the stratospheric ozone in the stratosphere, thus depleting the ozone layer, a natural UV filter. When in the troposphere, at elevated temperatures and in the presence of solar radiation, the VOC react with nitrogen oxides (NOx), generating the tropospheric ozone, which is a component of the smog. Regulations have been established to reduce the emissions of VOC from various sources, including products that contain solvents, in order to reduce the volume of the tropospheric ozone generated.

2. Substitution of hydrocarbon and chloroorganic solvents

The main alternative for the hydrocarbon solvents or their chloroorganic derivatives in the paint and varnish industry is oxygen-based alkyl-ether organic solvents. This is connected, among other things, with a dynamic growth in the share of production of water-based paints at the cost of solvent-based paints.

Alkyl ether solvents are a group of more than 30 compounds. As a rule, they are characterized by excellent biodegradability although their toxicological profiles are highly various. Taking into account EU legislation, the use and evaluation of glycol ethers ought to be viewed in the light of the European Directive 76-769 that relates to "limitations in the trade and use of hazardous substances and preparations", taking into consideration Categories 1 and 2 of products that are classified as being "toxic for reproduction". Part of the alkyl ether products under consideration belong in this class of products.

Manufacturers of paints are required to modify their product formulations in response to the requirements of restrictive laws, limiting the level of VOC's. This is one of the decisive criteria determining the directions of growth in the area, in addition to the economic factor.

There are three methods to reduce the level of VOC's in paints:

- developing paint formulations that contain coalescents other than those classified as VOC's (e.g., by using derivatives of iso-butyric aldehyde, such as Hydroxyester HE-1),
- developing paint formulations that contain coalescents and glycols classified as VOC's, in levels up to the limits established in applicable laws,
- developing paint formulations that contain no coalescents, by using alternative technologies for bonding the coating.

Paint formulations obtained without the use of coalescents are based on polymeric additives with low film formation temperatures (T_g) or on cross-linking polymers. On the other hand, production technologies for paints containing cross-linking polymers in the place of the coalescents are usually much more

expensive, compared with traditional resins while affecting the coating life as well as the toxicological parameters, and also they show other disadvantages of paints that contain polymers with low T_g. According to the published comprehensive comparison of the performance of water-based decorative paints, prepared by the Paint Research Association Coating Technology Centre as an independent, leading international organization in the paint and varnish industry, it is shown without doubt that the quality of coalescent-free paints is much deteriorated [1].

As an alternative to typical coalescent solvents, the market has offered so-called reactive coalescents that contain polyunsaturated fatty acid residues (e.g., those of sunflower oil). The solution is based on the concept of incorporation of the reactive coalescents in the structure of the coating formed by means of double bonds, rather than evaporation from the surface after the film formation. Archer RC from Archer Daniels Midland Company (ADM), USA, is the first and best known representative of the reactive coalescents for latex paints. From the point of view of chemistry, Archer RC is an ester of propylene glycol and sunflower oil acids. The reactive coalescent is safe for human health and is not classified as a VOC. However, the possibility of cross-linking the double bonds in the coating is questioned and there is evidence of serious deterioration of the quality of the resulting paint product, according to published literature reports. As a matter of fact, they serve as plasticizers rather than coalescents.

A majority of conventional coalescents that are present in the market have boiling points below the VOC criterion of 250^{o}C, thus being classified as the VOC category which involves applicable quantitative limitations. Several new products that are also offered have boiling points above the VOC criterion (Fig. 3).

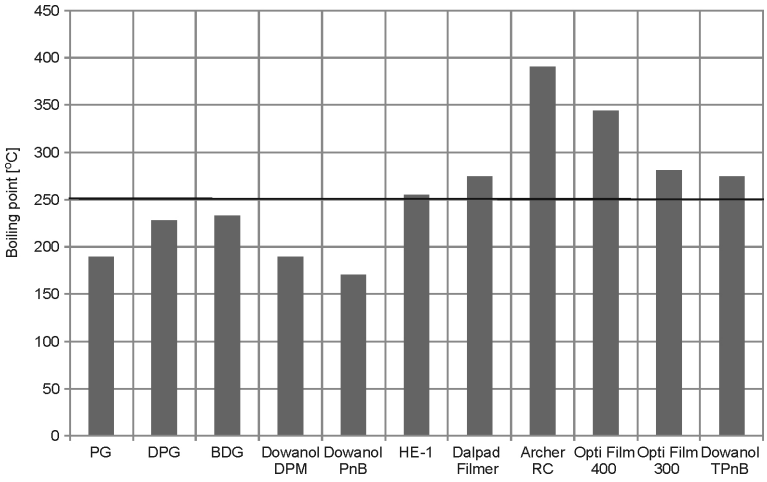


Fig. 3. Major organic solvents, used as coalescents in paint and varnish formulations

Hydroxyester HE-1 is the best identified new type of a coalescent which satisfies requirements for VOC's and of which the properties have been described in a most detailed manner. New proposals for coalescents having elevated boiling points, such as Dalpad Filmer, Opti Film 400, or Opti Film 300, are more expensive alternatives with shorter traditions of use. The paint quality may also be compromised in this case.

3. Legislation relating to the use of chemicals (reach)

Laws requiring reductions of the emissions of VOC's, imposed by the Council Directives 1999/13/EC and 2004/42/EC, have enabled reduction of the emissions of volatile solvents having boiling points of less than 250^0C. Other regulations relate to improvements in human health condition and environmental protection against the risks created by chemical substances, implementation of new methods for safety evaluation, and improvement in the scope of the safe use of and trading in chemical substances by all industries [5]. Thus, the new REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) of the European Parliament and the Council that came into force on 1 June 2007 (1907/2006/EC – REACH) relates to the safe use of chemical substances.

The new regulation introduces rules of registration and evaluation of chemical products and, in certain cases, also rules of authorization, restrictions, and use. According to the provisions of the EU Treaty, the REACH regulation is a direct obligation of every member state without having to include such regulations in their respective legislations. Before the REACH legislation package came into force, evaluation of the risk involved in the use of chemical substances, as well as preparation of information on the safety of their use were responsibility of state agencies and Community agencies. At present, this is a responsibility of respective industries. Manufacturers and importers of chemical substances are now obliged to evaluate information on the properties of their products and report such information (starting from 1 June 2008) to the central data base, operated by the European Chemicals Agency, based in Helsinki.

The REACH system is basically intended to make sure that chemicals used in consumer goods are safe for the human health and natural environment. More information about chemical compounds and their safe use ought to be collected to achieve the objective. Under the REACH system, manufacturers and importers of chemical compounds are required to register such compounds, report information about their uses, and provide evidence that it is possible to use them in a safe manner.

The following conditions must be satisfied in order to make REACH the first step to making Europe a safe and healthy environment:

- replacement of hazardous chemicals with their safer substitutes, if there are any,
- provision of relevant data on the safety of use of such chemicals and their substitutes,
- providing that the chemical industry shall be responsible for the safety of its products,
- establishing the consumer rights to information about any chemicals present in the products they buy.

Starting with the beginning of the year 2009, the entities concerned in a given chemical substance will establish a forum for exchange of information and then will be able to register such substances jointly, acting as members of a consortium, following evaluation of registration documents, specifically proposals to make extra tests. The agency will prepare decisions in the matter (starting with end of 2011), providing supplementary evaluation of high-risk substances.

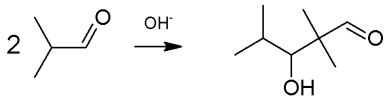
Certain uses of those substances that create the highest risk to human health and life will be subject to authorization starting from 2012. Applications for authorization must comprise an analysis of the possibilities and schedule for the substitution of a given chemical, or a R&D plan intended to select an alternative substance or technology (that raises a lesser amount of concern), as well as a social and economic analysis of the chemical substance.

The REACH system is not intended to require the registration of all chemical substances. Exceptions from the obligation to register chemical substances have been made for some industries, e.g., the food processing industry because the issue is addressed by Community legislation. For instance, food components that are subject to Regulation 178/2002 are not required to be registered under REACH, however, the use by the food processing industry of other chemical substances, such as those used for food packaging or purification, is subject to registration under REACH.

4. A concept to launch production of advanced coalescent solvents

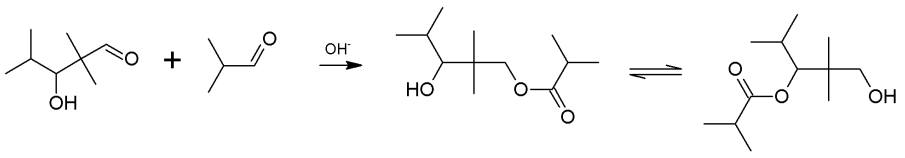
Hydroxyester HE-1 has been developed as an alternative to toxic solvents and coalescent used in the production of paints and varnishes. HE-1 is obtained from isobutanal in a sequence of chemical reactions (1, 2) in which isobutyric aldehyde (isobutanal) is the basic raw material in the process of aldol condensation followed by the Cannizaro and Tiszczenko's reaction:

- aldol condensation of 2 molecules of isobutanal



(1)

- condensation and disproportioning of isobutanal and aldol obtained in Step 1, according to the Canizzaro-Tiszczenko's mechanism



3-hydroxy-2,2,4-trimethylpentyl isobutyrate

3-hydroxy-2,2-dimethyl-1-(1-methylethyl)-propyl isobutyrate

The hydroxyester HE-1 is an isomeric, equimolar mixture of 3-hydroxy-2,2,4-trimethylpentyl isobutyrate and 3-hydroxy-2,2-dimethyl-1-(1-methylethyl)-propyl isobutyrate (1). It is a highly competitive coalescent for emulsion paints both in the aspects of economics and performance.

According to a commercially viable process of technology, this valuable chemical is obtained by catalytic trimerisation of isobutanal according to the Tiszczenko condensation reaction, referred to earlier in this paper.

HE-1 is a hydrophobic organic solvent which is mainly used as a coalescent in formulations of water-based paints for architectural coatings. The level of the coalescent in water-based paints is usually in the range from 2 to 5% [8].

Depending on the formal definitions and methods and criteria of evaluation, HE-1 is classified in various regions of the world either as VOC or not VOC. According to the EU Directive 2004/42/EC, adopting a boiling point of more than 250^{o}C for classification as other than VOC's, the Hydroxyester HE-1 is not classified as a Volatile Organic Compound. In the Chinese market, HE-1 is classified as a safe and environmentally friendly product. In the United States, HE-1 is regarded as a 100% Volatile Organic Compound according to the EPA standard, Method 24 [2, 7].

The concept to manufacture safe solvents and coalescents is based on the possibility of management of existing raw materials and facilities of the Oxo Plant in the "Kędzierzyn" Nitrogen Works in Kędzierzyn-Koźle. Given the expected limitations in the use of phthalate solvents made from isobutyric aldehyde, restructuring of the manufacturing process may be based on the use of isobutyric aldehyde to obtain the hydroxyester HE-1 [10].

The existing raw materials and facilities of the "Kędzierzyn" Nitrogen Works are sufficient to cover the entire national demand on advanced coalescents, which is assessed to be a minimum of 5,000 tones per year, plus exports. The assumption that HE-1 will be processed to obtain further derivatives justifies production growth to as many as several dozen thousand tons per year for the market of advanced solvents, plasticizers, and surfactants. The products concerned are the diester HE-1 with isobutyric acid, synthesis of isobutyl isobu-

tyrate, pentanediol, ethoxylated derivatives, and other products [9]. The target is launching an entire production complex for processing isobutyric aldehyde to obtain a number of advanced chemicals on which there is a great demand in the market.

Given the very good ecological evaluation of the said derivatives as well as the fact that requirements imposed by the EU legislation are fulfilled by such products, there exist conditions for the existing manufacturing potential and the available volumes of isobutyric aldehyde to be used in making advanced chemicals based on innovative Polish technology.

Two research projects relating to the subject are well under way in the Opole University of Technology, based on the raw materials and facilities of the Oxo Plant in the "Kędzierzyn" Nitrogen Works. It is planned that production of HE-1 is to be launched in two steps: the starting of a 2-3 thousand tons/year plant by the year 2010, followed by expansion of the plant capacity to 10 thousand tons/year at a later date.

This would enable replacement of alkyl ether-type of coalescent solvents having boiling points of less than 250^{o}C, and imports of less of the high volumes of such products being purchased outside the European Union at present.

The target is a more advanced technology, better product offer for the advanced chemical industry, and cutting emissions of the harmful chemicals classified as Volatile Organic Compounds by several to a dozen or so thousand tons per year.

In view of its envisaged marketing, the product is also subject to registration under REACH. As part of the R&D projects, toxicological and ecotoxicological tests are being made as necessary for the product registration, to comply with OECD requirements. The results so far indicate that the product has no toxic properties and is safe for use. The product was used as a coalescent in water-based paints formulations. Test results have been compared with those obtained for typical coalescents, and the performance results are evaluated as similar.

As part of evaluation of the toxicological and ecotoxicological properties of the Hydroxyester HE-1, tests that are required for the product certification under REACH [4, 6] have been carried out in the Institute for the Organic Industry, Department of Toxicological and Ecotoxicological Studies in Pszczyna, according to OECD guidelines. The scope of the tests included determination of the properties that are necessary for product registration.

Based on the test results it has been found that the test substance – Hydroxyester HE-1 – should be classified as one of Category 5 according to the rules of the Global Harmonised System (GHS). Based on the tests results obtained for the Hydroxyester HE-1 it was found that after running the test for 28 days the product was found to be 61.9% biodegradable, which is sufficient.

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PRODUKTY KONDENSACJI ALDEHYDU IZOMASŁOWEGO JAKO EKOLOGICZNE ROZPUSZCZALNIKI I KOALESCENTY FARB I LAKIERÓW

S t r e s z c z e n i e

Obszernie zróżnicowane chemicznie lotne związki organiczne i koalescenty zastępowane przez tzw. „zielone” rozpuszczalniki lub ciecze naturalnego pochodzenia o wysokiej temperaturze wrzenia. Wymagania dotyczące redukcji emisji lotnych związków organicznych (VOC) zostały narzucone przez prawo Unii Europejskiej i są adresowane przede wszystkim do producentów oraz importerów farb i lakierów. Poziom VOC w farbach może być zmniejszony poprzez stosowanie w recepturach farb rozpuszczalników i koalescentów nieklasyfikowanych jako VOC. Aby to osiągnąć, alkiloetery (klasyfikowane jako VOC) powszechnie stosowane w recepturach farb i lakierów wodorozcieńczalnych można zastąpić hydroksyesterem HE1, który nie jest zabroniony. Koncepcję uruchomienia produkcji bezpiecznych rozpuszczalników i koalescentów oparto na możliwości zagospodarowania istniejących zasobów surowcowych i zaplecza technicznego instalacji Oxo w Zakładach Azotowych Kędzierzyn S.A. Zaproponowany produkt jest bezpieczny w stosowaniu (nieklasyfikowany jako VOC) oraz nie wykazuje właściwości toksykologicznych i ekotoksykologicznych.

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