Using of the waste products as a source to production gel paint stripper

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Introduction

The elimination of by-products production is an important aspect of many nowadays technologies. However, sometimes we do not eliminate all products which are not used as direct product to synthesis the main product of this process. In this situation it is important to find another process, where the obtained by-products will be used as raw material or component of the final product. One of such processes is the Cyclopol technology, wherein by-products were used to obtain the components of the formulation for removing paint.

There are also processes and technologies where it is impossible to eliminate the generated waste. These include the process of paint removing, wherein the final product is a mixture of removed paint and the medium used for its removal.

In paint strippers produced nowadays, based on a organic solvent, such compounds as are used as an active substance: benzyl alcohol [1], alkylene carbonates [2], carboxylic acid esters [3 – 5], cyclic ethers [6] and many others [7]. In addition, such excipients as: co-solvents (low molecular weight alcohols, ketones, ethers), activators, evaporation retardants, thickeners or surfactants are added to preparations. The most of these compounds are specially prepared for this purpose. From the point of view of environmental protection, it is therefore preferable to apply to production of preparations for the removal of paint products generated in a single technology or technologies implemented in a single production plant. The example of that technology can be the Cyclopol process which is realized in Grupa Azoty S.A. in Tarnów. Cyclopol technology allows the synthesis of cyclohexanone from cyclohexane. It started in Zakłady Azotowe in Tarnów Mościce S.A. in 1974. The technology was modified in subsequent years to eliminate various technological problems [8 – 11]. But the changes have not eliminated all wastes and by-products generated in process. Some by-products, which are formed in distillation plant for separation of a mixture cyclohexanol – cyclohexanone, can be, after adequate preparation, used as a components to production of paint stripper. There are the *frakol* (alcohol fraction) and MKM (acid fraction). Frakol is mixture of alcohol and cyclic compounds with low water content. It is exuded from cyclohexanol – cyclohexanone stream in distillation process. The main alcohol in this mixture is n-pentanol (50 – 70%) [12]. MKM is exuded at stage of hydrolysis products of oxidation cyclohexane separation. The main components of this mixture are: valeric acid (52 – 60%), butyric acid (10 – 14%), caproic acid (8 – 12%), propionic acid (2 – 3%), acetic acid (0,4 – 0,8%), formic acid (0,1 – 0,2%) and high molecular weight organic compounds (10%) [12].

Materials and methods

We can use alcohol fraction *frakol*, without additional treatment, to obtain the paint stripper. To apply the second of by-products, fraction of the monocarboxylic acid, we must obtain the mixture of esters. The ester solvent is prepared by esterification process with alcohol fraction and acid fraction. The ester solvent is appropriate component of preparation. Description synthesis of ester solvent was shown in previous paper [13].

In the presented study the influence of boiling point of the ester solvent on utility properties of gel paint stripper was studied.

In study the esterification of two waste fraction from Cyclopol process was conducted. It was alcohol fraction *frakol* and fraction of monocarboxylic acid MKM. The esterification was conducted at weight ratio of alcohol:acid fraction 1.75:1. The process was carried out for 10 hours in the presence of sulphuric acid (1 wt. %) as a catalyst. The water generated in the esterification, was continuously evacuated by azeotropic distillation. After the end of esterification process, the obtained mixture was separated by distillation. The distillation was conducted collecting the fractions at different temperature range. The distillate contained mostly esters and unreacted alcohols. During the first esterification fraction 1.1 was collected in temperature range from 50 to 140°C. During the second esterification the ester solvent was divided on 3 fractions with different boiling range. Fraction 2.1 from 45 to 65°C, fraction 2.2 from 90 to 130°C and fraction 2.3 from 130 to 140°C. In next esterification the ester solvent was divided on two fractions, fraction 3.1 with boiling range from 90 to 120°C and fraction 3.2 with boiling range from 120 to 140°C.

Table 1

The boiling range for individual fractions

Fraction	Boiling range, °C
1.1	50 – 140
2.1	45 – 65
2.2	90 – 130
2.3	130 – 140
3.1	90 – 120
3.2	120 – 140

GC analysis of obtained solvents was performed. The chromatographic test was performed by Gas chromatograph SRI 8610C, using the column MXT 502.2 60 meters 0.53 mm. The initial temperature was 80°C and was rising 10°C per minute to 120°C, next temperature was rising 20°C per minute to 200°C. Temperature of 200°C was maintained for 15 minutes..

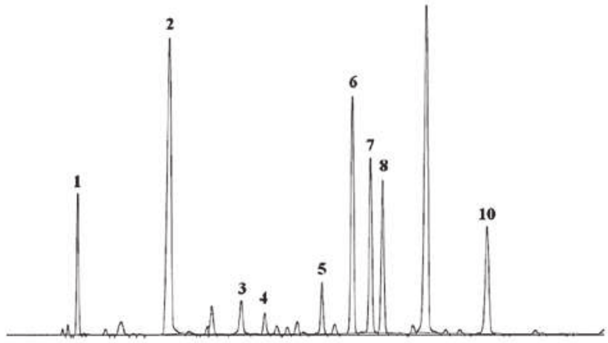

Fig. 1. The chromatogram of fraction 1.1

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Peaks assignation based on reference chromatogram: (1) unidentified peak; (2) pentanol; (3) pentyl formate; (4) 2-metylocyklopentanon; (5) pentyl acetate; (6) pentyl propionate; (7) dipentyl ether; (8) pentyl butyrate; (9) pentyl valerate; (10) pentyl caproate.

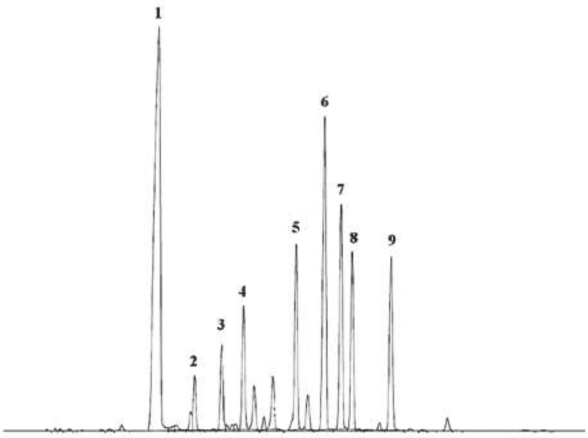

Fig. 2. The chromatogram of fraction 3.1

Similarly peaks assignation based on reference chromatogram: (1) pentanol; (2) unidentified peak; (3) pentyl formate; (4) 2-metylocyklopentanon; (5) pentyl acetate; (6) pentyl propionate; (7) dipentyl ether; (8) pentyl butyrate; (9) pentyl valerate;

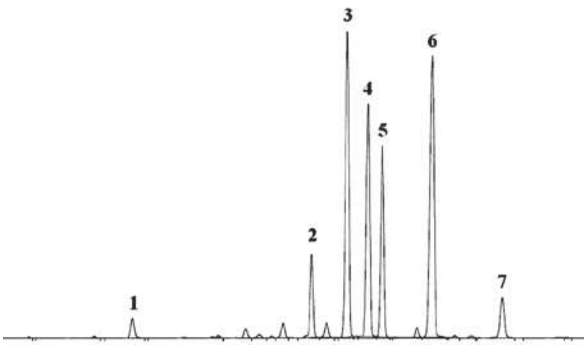

Fig. 3. The chromatogram of fraction 3.2

Also in this case the peaks assignation based on reference chromatogram: (1) pentanol; (2) pentyl acetate; (3) pentyl propionate; (4) dipentyl ether; (5) pentyl butyrate; (6) pentyl valerate; (7) pentyl caproate.

Next the series of paint strippers was prepared. The constant components of formulations were: active ingredients contain dioksolan in amount of 45% and alcohol fraction frakol in amount of 14%; rheology regulator – methylhydroxypropylcellulose in amount of 5% and additives, hydrogen peroxide–urea adduct and distilled water in amount of 14.5%. Active ingredient, which was changed in individual compositions, was ester fractions with different boiling range. These fractions were used in amount of 7%.

The fractions used to obtain the paint remover were chosen based on chromatographic test. Fractions 1.1 (Formulation I), 2.2 (Formulation II), 2.3 Formulation III) and 3.1 (Formulation D) were selected. Next three formulations, with mixtures fraction of 2.2, 3.1 and 3.2, were prepared. The compositions of these formulation are shown in Table 2.

After prepared of each formulation the stability and effectiveness of action were rated. The study of effectiveness of action was conducted on plates from different kind of materials (wood, metal). The wood plate was painted the several layers of oil-alkyd enamel. Age of outer coating is estimated to be 12 years. The metal plate was painted anticorrosion coating and three layers of acrylic varnish which are used to paint the bus in MAN factory. Age of the coatings was 2.5 years. The preparation was put on the plate. After 30 minutes, in the case of wooden plate and 24 hours, in the case of metal plates, the preparation was removed and quality of remove was rated. Effectiveness studies were performed immediately after receiving the formulation.

Table 2
The amount of ester fraction used to prepare various preparations

Ester fraction	Preparation						
	I	II	III	A	B	C	D
	Content,% wt.						
1.1	7	-	-	-	-	-	-
2.2	-	7	-	3.5	3.5	3.5	-
2.3	-	-	7	-	-	-	-
3.1	-	-	-	3.5	-	1.75	7
3.2	-	-	-	-	3.5	1.75	-
Total ester mixture	7	7	7	7	7	7	7

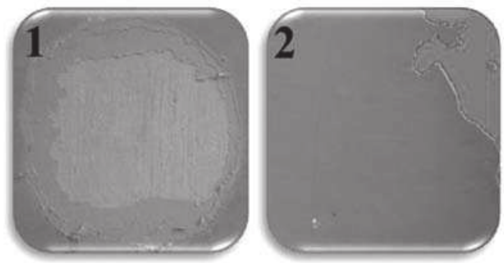

Fig. 4. Effect of action of formulation D on (1) wooden and (2) metal plate

Results and discussion

The GC assay shows that obtained ester solvents consists of mainly unreacted pentyl alcohol and its esters. In the depending on boiling range, fractions differ in the content of the individual components. In fractions received in range from 120 to 140°C the main components are pentyl esters (pentyl formate, pentyl acetate, pentyl propionate, butyrate, pentyl valerate, pentyl hexanoate). Whereas in fraction received in range from 90 to 120°C the main components are pentyl esters and significant amount of unreacted alcohol pentyl.

Formulation I, which was obtained using fraction 1.1 delaminated after approx. 24 hours of preparation. Similarly formulation II, which was obtained using fraction 2.2 delaminated after approx. 48 hours. Both formulation I and II after re-mixing did not take a gel form. Formulation A, which was obtained using a mixture of fractions of 2.2 and 3.1 was showing stability for approximately two weeks from preparation. After this time the formulation started to delaminate. After re-mixing formulation took gel form, which was lasting for about 24 hours. After this time the formulation started to delaminate. Only formulation D, which was obtained using fraction 3.1 was stable for about three months.

In conducted study we failed to obtain stable preparation containing a fraction 2.3 (Formulation I). Similarly, formulations B and C which was obtained using a mixture of fractions of 2.2 and 3.2 and fractions 2.2, 3.1, 3.2 delaminated immediately after the obtain.

Effectiveness of action studies were performed immediately after receiving the formulation. To study products, which had gel form, were selected. All tested formulations showed high efficacy in removing coatings. It caused wrinkling of the shell making it easier to remove. Moreover, the formulations removed all layers applied coating.

Table 3

Effect of action of the formulations on the plate

Composition	Effect of action	
	Wooden plate	Metal plate
Composition I	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.
Composition II	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.
Composition III	The preparation delaminated	
Composition A	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.
Composition B	The preparation delaminated	
Composition C	The preparation delaminated	
Composition D	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.	Formulation causes wrinkling of the shell making it easier to remove. It removes all layers of paint.

Summary and conclusions

The study shows significant influence of boiling point of ester solvent on stability of obtained paint strippers. Direct influence on the stability of gel has a content of unreacted alcohol pentyl originating from fraction *frakol*. Based on conducted study it can be said that to maintain a stable formulation requires presence of unreacted alcohol pentyl. Too high concentration of esters, or to low concentration of pentyl alcohol in the formulation causes its delamination.

Based on the results, the boiling range, which should be received ester fraction (the preparation was stable) was specified on 90 to 120°C. The study shows that reduction of esters does not cause lowering efficacy of preparation. The study shows that after adequate preparation, selected waste fractions derived from technology Cyklopol can be use as components stable gel paint strippers with a high efficiency designed to remove old coatings type in oil-alkyd enamel and acrylic coatings.

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