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Application of the side stream from the Cyklopol process in paint stripping formulations

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The utilization of two side streams from the Cyklopol process was studied. The first one is the monohydric alcohols fraction and the second one is the fraction of mono-carboxylic acids. We propose to utilize these fractions and their esters as a component of gel formulation painting remover. Our composites have a gel formulation suitable for easy application on a vertical surface. D-DBS (1,3:2,4-Di-O-benzylidene-D-sorbitol) or MHPC (methylhydroxypropylcellulose) were used as gelling agents for organic liquids. The D-DBS compound is characterized by transparency and reduced yellowing of composition. The properties of the obtained preparations were compared to the properties of commercially available gel formulations SCANSOL and STRIPER.
Our initial investigations indicate that side streams from the Cyklopol process are good and cheap resources of raw materials for the preparation of paint stripping formulations.

Keywords: Cyklopol, side stream, paint removing, gel formulation.

INTRODUCTION

Various types of protective coatings are applied to secure objects or their parts against weather conditions or aggressive environments attacks. In most cases varnish coatings are used as the protective coatings. Unfortunately, the characteristics of these coatings is ageing with time and sensitivity to mechanical damage. Therefore, they require periodic renewal. To ensure a long term of elements protection, the old layers of paint must be removed before putting on the new coatings. Also in the case of defective painting of the new elements it becomes a necessity to clean the painted surface without mechanical damage of the base. Coating must also be removed before various repairs (welding, soldering, cementing). Deleting individual layers of coatings without damaging the bottom layers of paint is a problem of a different nature. This situation occurs when graffiti must be cleaned from the surface.

It is generally known that the mechanical, thermal and chemical methods of stripping which depend on the nature of the factor were used for the degradation of the coating[1]. Each of these methods has advantages and disadvantages. These are concerned with a various degree of surface resistance to the aggressiveness of the method used, the ability to reach the not easily accessible items, environmental considerations, etc. The chemical methods used gel preparations and it seems to be the most universal. Therefore, in recent years the number of products from this group available on the market has increased.

Nowadays, methylene chloride is one of the main substances used to remove coatings because of its power of dissolving and stripping off coatings from the surface. It is also reasonably priced as it is the waste from the production of some pharmaceuticals and food dyes (e.g. Lycopene[2], the strongest known plant antioxidant, yield of tomatoes by solvent extraction[3,4]). However, due to other properties (limited evidence of carcinogenicity, impact on the ozone layer, phosgene and hydrogen chloride emissions during combustion, and high toxicity for aquatic organisms) it is an undesirable component[5,6] and must be replaced with other substances which have a smaller impact on the natural environment.

Lasting for years searching for ingredients that could replace methylene chloride still has not led to finding an equally cheap and effective solvent. Comparative studies of preparations containing and not containing methylene chloride show that the elimination of the chemical composition results in significant lengthening of the time required for the penetration and thus the time to remove the coating[7]. The substances with stripping properties similar to those of methylene chloride are more expensive. The reduction costs of methylene chloride-free composition for coatings removal can be achieved by using cheap raw materials for a synthesis of other components which are by-products of different chemical processes.

Our researches showed that some by-product fractions from the Cyklopol process contain the solvents actively working on the paint film. These fractions may constitute an attractive raw material for the preparations without methylene chloride.

In the preparations for removing coatings, which enable their application to vertical surfaces the thickening and gelling agents are present. Both compounds increase the viscosity of the preparation and hinder the evaporation of volatile solvents. In many cases, their application allows for better utilization of active compounds of the preparation[10]. The examples of the substances used for this purpose are gelatine, gum arabic E414, tragacanth E413, guar gum E412, starch, agar, xanthine E415, methylcellulose and its derivatives[11].

In an environment of polyhydric alcohol gels resistant to other organic solvents creates sorbitol acetal derivative - dibenzylidene sorbitol (1,3:2,4-di-O-benzylidene--D-sorbitol)[11,12].

In this work, new formula of the preparation for coating removal containing mentioned above D-DBS (1,3:2,4-di-O-benzylideno-D-sorbitol) and MHPC (methylhydroxypropylcellulose) have been investigated.

EXPERIMENTAL

In the work two by-product fractions from the Cyklopol process were used. The first one was Frakol, a monohydric alcohols composition, and the second one was MKM, a mono-carboxylic acids composition. Both originated from Zakłady Azotowe in Tarnów-Mościce S.A.

Using the industrial waste fractions described above, two kinds of solvents were prepared. The first solvent (donated as Solvent 1) was prepared by Frakol esterified with MKM fraction. The weight ratio of Frakol:MKM was 2:1. The process was carried out for 5 hours in the presence of sulphuric acid (1 wt. %) as a catalyst, in a temperature range of 105 to 150°C. The water generated in the esterification, was continuously evacuated by azeotropic distillation. After finishing the esterification process the obtained mixture was separated by vacuum distillation (0.0027 MPa, T = 90°C).

To reduce the average boiling point of the preparation ingredients, we used another solvent (Solvent 2) that was obtained in the esterification of Frakol by acetic acid anhydride. The method of obtaining Solvent 2 was described elsewhere[9]. The boiling temperature of this solvent was between 90 to 150°C (at 0.1013 MPa).

Using the above prepared solvents (Solvent 1 and Solvent 2) the preparation to varnish coatings was obtained. In this case, the ingredients reported in Table 1 were varied in terms of their chemical properties. Frakol and glycerine were placed in a glass reactor together with a thickening agent (D-DBS or MHPC) and homogenized.

In a separate glass reactor Solvent 1 and Solvent 2 were mixed with N-methyl-pyrrolidone and an activator (methylene chloride). Paraffin used in the preparation was dissolved in petroleum ether. After that the ingredients were mixed and homogenized for 20 minutes (13 000 rpm). The average composition of preparations is given in Table 1. The obtained mixture was allowed to stand for 48 hours at room temperature, and next it was used to remove coatings.

Table 1. Average composition of preparations

Ingredients	Average content (wt%)
Methylene chloride	26.0
Solvent 1	16.0
Solvent 2	12.0
Frakol	10.0
Petroleum ether	4.0
Glycerol	20.0
Solid paraffin	1.0
N-methyl-2-pyrrolidone	8.0
D-DBS or MHPC - thickening agents	3.0

The functional quality of the new formulations was investigated on the plates of metal and wood covering various types of varnish coatings. As a reference, the commercially available preparations, including Striper® (PPUH „WAMA"), Rust-Oleum® (Netherlands B.V.) and Scansol® (Scandia Cosmetics S.A) were used. During the test of paint strippers, the contact time with the purified surface was 20 minutes. The effects of preparations for horizontal and vertical surfaces were evaluated.

All components were determined by GC-MS method, using Agilent 6890N chromatograph equipped with 5975C inert XL MSD detector, HP-5MS 0.25 mm column – 30 m long using following GC conditions: split 50:1; injector temperature 280°C; initial temperature 40°C, rate 5°C·min^{-1}, final temperature 270°C for 30 min (total time 100 min). The compounds were identified based on the mass spectra NIST 95 library and the base of SDBS[8].

The D-DBS (1,3:2,4-Di-O-benzylideno-D-sorbitol) used in this study was produced by the Hangzhou Dayangchem Co., Ltd, Davis Group, while the MHPC (methylhydroxypropylcellulose) was made by Scandia Cosmetics S.A. in Niepołomice. The latter one was used as a thickening agent in the commercially manufactured preparations to remove coatings.

Other ingredients used in the studies were pure chemical reagents, e.g. glycerol, N-methylpyrrolidone, acetic anhydride, sulphuric acid and methylene chloride.

RESULTS AND DISCUSSION

Preparation of ingredients based on the west fraction from Cyklopol

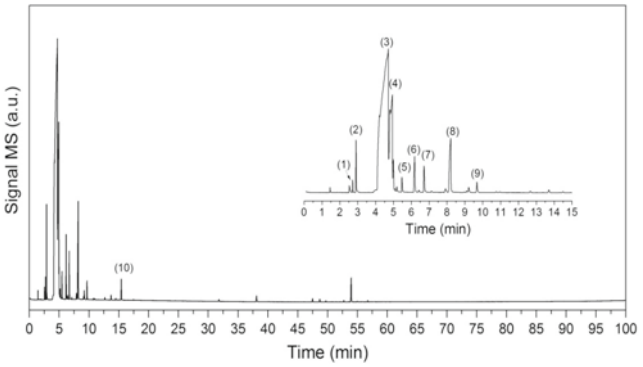

Figure 1. The chromatograms of dry Frakol. Designations based on NIST Library: (1) Cyclohexene; (2) Pentanal; (3) 1-Pentanol; (4) Cyclopentanol; (5) 7-Oxabicyclo[2.2.1]heptane; (6) 2-methylcyclopentanone; (7) 7-Oxabicyclo[4.1.0]heptane; (8) Cyclohexanone; (9) Ethoxycyclohexane; (10) 1-Cyclohexylbutane

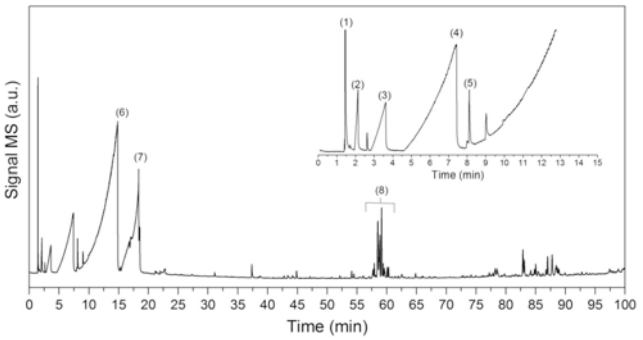

Figure 2. The chromatograms of MKM fraction. Peaks assignation based on NIST Library: (1) Water; (2) Acetic acid; (3) Propanoic acid; (4) Butanoic acid; (5) Cyclohexanone; (6) Pentanoic acid and (7) Hexanoic acid (8) Unidentified peaks

First, the compositions of Frakol and MKM waste fractions were determined by GC-MS. The obtained chromatograms are displayed in Figures 1 and 2.

Based on the mass spectra NIST 95 Library it was identified that in the Frakol fraction the main compounds are cyclopentene, pentan-1-ol, cyclopentanol, 7-Oxabicyclo[4.1.0]heptane and cyclohexanone (Fig. 1). In contrast, butanoic, pentanoic and hexanoic acids are the primary compounds presented in the MKM fraction (Fig. 2). In the latter fraction small amounts of acetic and propanoic acids have been determined as well.

Figure 3 shows the chromatogram obtained for the fraction boiling at 90–170°C at 0.1013 MPa. It is clear that after esterification there are no more acids in the mixture which are fully converted into various esters (in Fig. 3 description). Since in the esterification process an excess of the Frakol fraction is used in Solvent 1, the

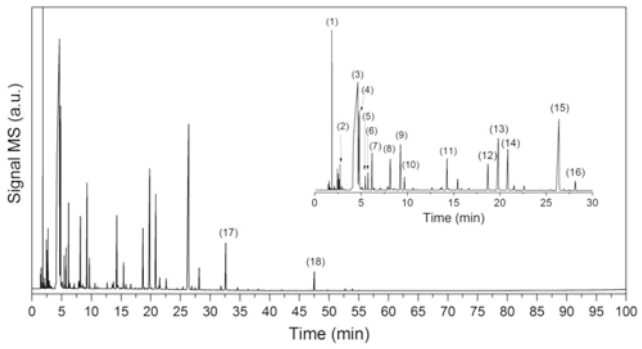

Figure 3. The chromatogram of Solvent 1. Peaks assignation based on NIST Library: (1) Cyclopentene; (2) Cyclohexene; (3) 1-Pentanol; (4) Cyclopentanol; (5) 7-Oxabicyclo[2.2.1]heptane; (6) 1-Pentyl formate (7) 2-methylcyclopentanone; (8) Cyclohexanone; (9) 1-Pentyl acetate; (10) Ethoxycyclohexane; (11) 1-Hexyl propionate; (12) 1,1'-oxybis Pentane (13) 1-pentyl butanoate; (14) Unidentified peak; (15) 1-Pentyl pentanoate; (16) Cyclopentyl pentanoate and (17) 1-Pentyl hexanoate (18) Unidentified peak

unreacted alcohols, mainly 1-pentanol and cyclopentanol, are also present. In addition, ketones, such as cyclohexanone, 2-methyl-cyclopentanone, cyclic alkenes and various ethers were found in the mixture.

An exemplary chromatogram of Solvent 2 is shown in Figure 4. The major components detected by GC-MS

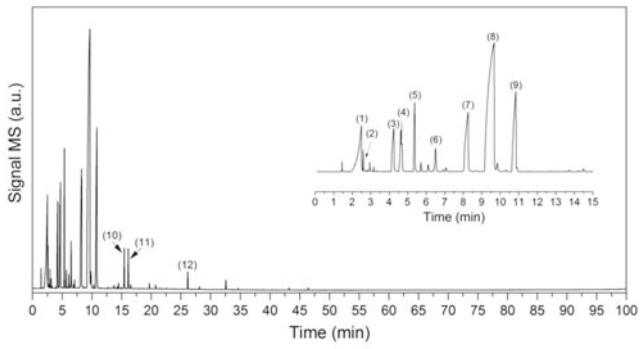

Figure 4. Chromatogram of Solvent 2. Peaks assignation based on NIST Library: (1) Acetic acid; (2) 1-Butanol; (3) 1-Pentanol; (4) Cyclopentanol; (5) 1-Butyl acetate; (6) 2-Pentyl acetate; (7) Cyclohexanone; (8) 1-Pentyl acetate; (9) Cyclopentyl acetate; (10) Unidentified peak; (11) Cyclohexyl acetate and (12) 1-Pentyl pentanoate

are 1-butyl acetate, 1-pentyl and cyclopentyl acetate, unreacted alcohols (pentan-1-ol and cyclopentanol) and acetic acid, as well as ketones, such as cyclopentanone and cyclohexanone.

Table 2. Comparison of the properties of various preparations for varnish coatings

Preparations	Observations
1 (with D-DBS)	slightly softens the coating; maintained on the vertical surface
2 (with MHPC)	slightly softens the coating; flows down the vertical surface
Striper®	causes swelling and wrinkling of the shell; maintained on the vertical surface
Rust-Oleum®	causes swelling and wrinkling of the shell; flows down the vertical surface
Scansol®	causes swelling and wrinkling of the shell; maintained on the vertical surface

Tests of preparations

The results of observations are summarized in Table 2.

The preparation containing D-DBS forms a gel whose consistency is similar to that of the commercially available preparations. In contrast, the MHPC-containing preparation does not form a good gel, thus the preparation flows down a vertical surface.

The obtained preparation exhibits slightly worse properties than the commercial preparations. Their application needs a longer contact time with varnish coatings.

CONCLUSIONS

The Cyklopol waste fractions contain alcohols, ketones and acids. The synthesized solvents are a mixture of chemical compounds, in which esters are the main components. Esters, especially such as pentyl acetate, play the role of resin solvents in fast drying paints and polyurethane varnishes. Alcohols perform a function of solvents, softeners of the coat paint and they improve the penetration effect of the mixture. They increase the swelling effect of colloids contained in the mixture and gel forming, too. This type of alcohols is often used as an additive to solvents for epoxy-, nitro-, and water-based paints. Ketones, like cyclohexanone, are good solvents for various organic compounds which are ingredients of nitrocellulose and two-component chemical hardening paints. Finally, paraffin, glycerol and thickening agents as well as gelling agents act as solvent evaporation retardants.

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