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## ACTIVE INGREDIENTS IN PAINT STRIPPERS

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### SUBSTANCJE AKTYWNE W PREPARATACH DO USUWANIA POWŁOK LAKIERNICZYCH

#### Abstract

The papers presents the study on the application of acetals as active ingredients in paint strippers. The formulation was prepared and the ability to wrinkling of the shell was rated. The ability to wrinkling of the shell was rated by examining the force required to detachment the coating.

**Keywords:** paint stripper, active ingredients, acetals

#### Streszczenie

W artykule przedstawiono badania dotyczące zastosowania acetalu jako substancji aktywnych w preparatach do usuwania powłok lakierniczych. Sporządzono preparaty oraz oceniono ich zdolność do odpajania powłoki. Zdolność do odpajania powłoki oceniano badając siłę potrzebną do oderwania powłoki.

**Słowa kluczowe:** preparaty do usuwania powłok lakierniczych, substancje aktywne, acetale

## 1. Introduction

Since the Council of the European Union has banned the use of methylene chloride in paint removers [1], it was necessary to find substances, which are able to replace this compound. Currently, active ingredients that are used include compounds, such as N-methylpyrrolidone [2–6] and benzyl alcohol [7–12] as well as alkylene carbonates, such as propylene carbonate or ethylene carbonate [13–15]. Furthermore, carboxylic acid esters are also used. In patents, benzoic acid methyl ester [16] as well as methyl esters of dicarboxylic acids, such as succinic acid, glutaric acid and adipic acid [17–19], are described. Moreover we can use such esters like: ethyl acetate, butyl acetate, ethyl 3-ethoxypropionate and 1-methoxy-2-propyl acetate. However, the most preferred is ethyl 3-ethoxypropionate [20, 21]. The patents also describe such compounds as alkyl derivatives of carboxylic acid amides, dicarboxylic acid and hydroxycarboxylic acids [22], alkoxyated aromatic alcohols [23, 34].

Research on this topic is also being conducted at the Institute of Organic Chemistry and Technology of the Department of Chemical Engineering and Technology at the Cracow University of Technology. In our research, we study the usefulness of acetals as active ingredients.

The topic of this study was to check the influence of different active substances from the group of acetals on the ability to remove the coating. For comparison, we used the most commonly used active ingredients (N-methylpyrrolidone and benzyl alcohol).

## 2. Materials and methods

### 2.1. The paint removers

In the study, paint removers based on the author's recipe were used. The way of their preparation was different for the used active ingredient. For the study, we used substances with a different partition coefficient (logP). Due to the used different active ingredients, we used preparations in two forms - gel and emulsion..

In the study, the following substances were used: N-methylpyrrolidone (logP -0.40), dimethoxymethane (logP -0.26), dioxolane (logP -0.06), benzyl alcohol (logP 1.03), diethoxyethane (logP 1.14), cyclohexanone ethylene ketal (logP 1.35), benzaldehyde ethylene acetal (logP 1.63), dipropoxyethane (logP 2.21), dibutoxyethane (logP 3.27).

### 2.2. Preparations in gel form

Dioxolane and N-methylpyrrolidone were used in the gel preparation as active ingredients.

**Table 1.** The composition of the gel preparation

Substance	Composition [% wt.]
Active ingredient	42.2
Adduct	14.0
Water	14.0
Frakol	13.5
Ester solvent	6.7
Modisurf Clarity	4.8
Methocel	4.8

### 2.3. Preparations in emulsion form

**Table 2.** The composition of the emulsion preparation

Substance	Composition [% wt.]
Active ingredient	45.6
Methyl esters of rapeseed oil	13.6
Hydrogen peroxide	13.6
Candelila wax	9.1
Ester solvent	6.8
Frakol	6.8
Tween 40	2.9
Glycerol monostearate	1.6

Dimethoxymethane, dioxolane, benzyl alcohol, diethoxyethane, cyclohexanone ethylene ketal, benzaldehyde ethylene acetal, dipropoxyethane, dibutoxyethane were used in the emulsion preparation as active ingredients.

### 2.4. Plates

In the study, we used five types of plates. Two plates (blue, white) were delivered by Fiat Auto Poland Company in Tychy. The blue plate was painted with solvent-based acrylic paint. The white plate was painted with waterborne acrylic paint. The other two plates (green and brown) were painted with melamine formaldehyde paints. The last plate (epoxy) was painted with epoxy paint. The three last paints are used for roof covering.



## 2.5. The study of coating detachment

The paint remover was applied on the plate. In each case, the formulation was applied to the surface of  $9 \pm 0.3 \text{ cm}^2$ . Due to the next steps of the procedure, we adopted a uniform square shape for the area of application of the preparation. The preparation was left on the surface for 24 hours. After this time, the preparation was removed and the effect on the surface was rated. A metal badge with an area of  $9 \pm 0.3 \text{ cm}^2$  was glued next to the coating. The glue was left for 48 hours to dry completely. After this time, the force required to detach the coating was measured. The measurement was performed on Zwick 1445 apparatus intended for testing the strength of materials. In the study, a constant crosshead speed of 50 mm/min was applied.

## 3. Results and discussion

### 3.1. Results of study of the interaction on the coating

In the case of the green plate, all active ingredients caused wrinkling of the shell. A similar situation took place in the case of the brown plate. An exception was diethoxyethane, which did not cause wrinkling of the shell. A different situation occurred in the case of the blue, white and epoxy plates. In those cases, wrinkling of the shell caused only dioxolane (emulsion). The wrinkling of the shell also caused dimethoxymethane, but only in the case of the blue plate. In the case of the epoxy plate, wrinkling of the shell also caused the preparation with benzyl alcohol. In other cases, the preparation did not cause any wrinkling of the shell.

### 3.2. Results of coating detachment study

In the case of the blue plate, we can see a reduction of the force needed to detach the coating that treated the preparation compared to the coating that did not treat the preparation. The average force required to pull-off the coating, which did not treat the preparation, is 216 N. However, not all layers of the coating are detached. The detachment of all layers of the coating was possible after the action on the coating formulations containing dioxolane (gel), diethoxyethane and benzaldehyde ethylene acetal. The force required to pull-off the coating is 158 N for dioxolane, 182 N for diethoxyethane and 136 N for benzaldehyde ethylene acetal. The preparations with cyclohexanone ethylene ketal and dibutoxyethane caused softening of the shell. It makes it possible to detach the coating of the silver layer with an average force of 148 N for cyclohexanone ethylene ketal and 121 N for dibutoxyethane.

Comparing the results with the properties of the compound (partition coefficient of o/w logP), we can see that, with an increase of the partition coefficient, the susceptibility to wrinkling of the shell is lower. The preparations containing dioxolane (logP -0.06) and

dimethoxymethane ( $\log P -0.26$ ) caused wrinkling of the shell. The preparations containing diethoxyethane ( $\log P 1.14$ ) and benzaldehyde ethylene acetal ( $\log P 1.63$ ) caused softening of the shell. This makes it possible to detach all layers of the coating. The preparations containing dipropoxyethane ( $\log P 2.21$ ) and dibutoxyethane ( $\log P 3.27$ ) also caused softening of the shell, but this makes possible to detach only one layer of the coating.

## Blue plate

**Table 3.** Results of coating detachment study for the blue plate

Active ingredient	Force		Comments
	kPa	N	
–	246.1	216.0	A part of the coating was detached
Dimethoxymethane	The coating was wrinkled		
Dioxolane (gel)	176.2	158.6	All layers of the coating were detached
Dioxolane (emulsion)	The coating was wrinkled		
Diethoxyethane	209.5	182.2	All layers of the coating were detached
Cyclohexanone ethylene ketal	159.0	147.9	All layers of the coating were partially detached
Benzaldehyde ethylene acetal	146.6	136.4	All layers of the coating were detached
Dipropoxyethane	147.9	133.1	Coating intact
Dibutoxyethane	139.5	121.4	Coating was detached to the silver layer

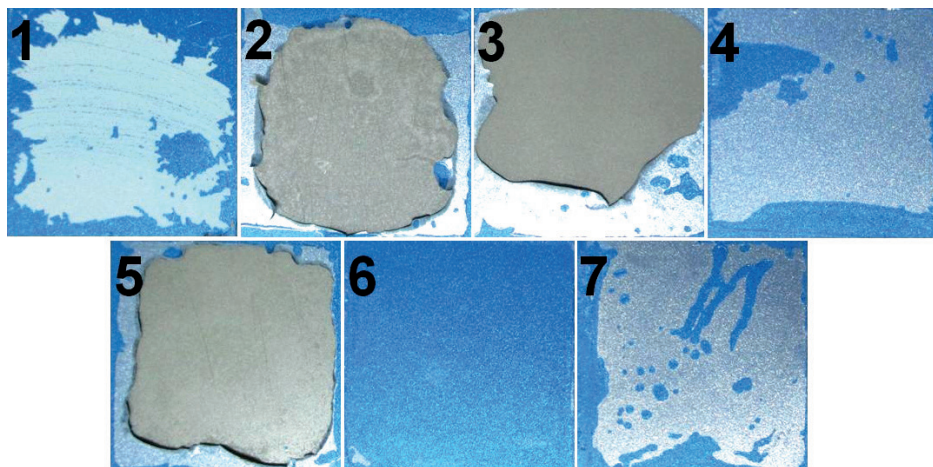


Fig. 1. The plate after study of coating detachment; 1 – reference sample, plate treated the preparation with 2 – dioxolane (gel), 3 – diethoxyethane, 4 – cyclohexanone ethylene ketal, 5 – benzaldehyde ethylene acetal, 6 – dipropoxyethane, 7 – dibutoxyethane

## White plate

**Table 4.** Results of coating detachment study for the white plate

Active ingredient	Force		Comments
	kPa	N	
–	269.0	242.1	Coating intact
N-methylpyrrolidone	226.4	197.0	The first layer of the coating was detached
Dimethoxymethane	162.3	151.0	All layers of the coating were detached
Dioxolane (gel)	306.3	284.9	Coating intact
Dioxolane (emulsion)	The coating was wrinkled		
Benzyl alcohol	152.9	142.2	All layers of the coating were detached
Diethoxyethane	63.0	56.6	All layers of the coating were detached
Cyclohexanone ethylene ketal	243.5	226.4	All layers of the coating were detached
Benzaldehyde ethylene acetal	358.2	333.1	All layers of the coating were partially detached
Dipropoxyethane	155.7	140.2	Coating intact
Dibutoxyethane	209.8	195.2	Coating intact

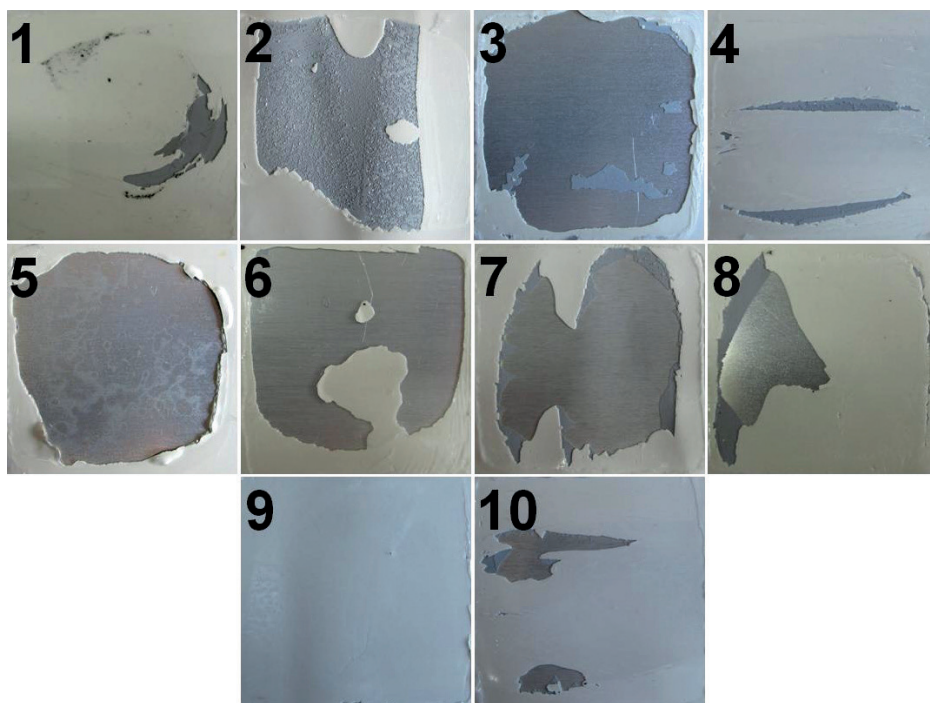


Fig. 2. The plate after study of coating detachment; 1 – reference sample, plate treated the preparation with 2 – N-methylpyrrolidone, 3 – dimethoxymethane 4 – dioxolane (gel), 5 – benzyl alcohol 6 – diethoxyethane, 7 – cyclohexanone ethylene ketal, 8 – benzaldehyde ethylene acetal, 9 – ipropoxyethane, 10 – dibutoxyethane



In the case of the white plate only, dioxolane (emulsion) caused wrinkling of the shell. In four causes, the activity caused softening of the shell, making the detachment of the coating possible. We can see that, with increasing logP, the force, which is needed to detach the coating, increases from 151 N for dimethoxymethane (logP -0.26) to 333 N for benzaldehyde ethylene acetal (logP 1.63). The exception is diethoxyethane. For this compound, the force needed to detach the coating is 56.6 N. A further increase of logP makes the preparation not soften the coating. In this case, the adhesion forces of the paint to the base are stronger than the adhesion forces of the glue to the coating. Therefore, we cannot detach the whole shell, but only small fragments. Such a situation took place in the case of the reference sample and the sample with dipropoxyethane and dibutoxyethane.

### Green plate

In the case of the green plate, all substances caused a significant reduction of the forces required to detach the coating. Only the preparation with N-methylpyrrolidone did not cause a reduction of the forces required to detach the coating. However, it softened the coating, making it possible to remove all of the top layer.

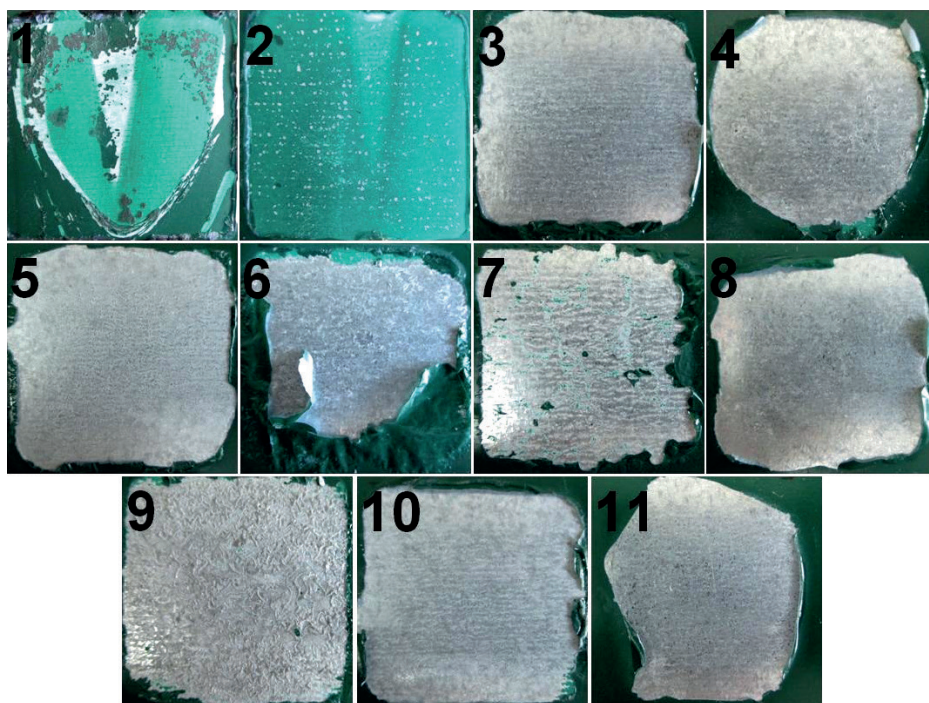


Fig. 3. The plate after study of coating detachment; 1 – reference sample, plate treated the preparation with 2 – N-methylpyrrolidone, 3 – dimethoxymethane 4 – dioxolane (gel), 5 – dioxolane (emulsion), 6 – benzyl alcohol 7 – diethoxyethane, 8 – cyclohexanone ethylene ketal, 9 – benzaldehyde ethylene acetal, 10 – dipropoxyethane, 11 – dibutoxyethane

In this case, regardless of the partition coefficient, the substances caused wrinkling of the shell. The only exception is N-methylpyrrolidone. In its case, despite a low value of partition coefficient, it did not cause wrinkling of the shell.

**Table 5.** Results of coating detachment study for the green plate

Active ingredient	Force		Comments
	kPa	N	
–	513.7	446.8	A part of the coating was detached
N-methylpyrrolidone	567.4	510.7	The first layer of the coating was detached
Dimethoxymethane	37.3	33.5	The coating was wrinkled
Dioxolane (gel)	139.1	121.0	The coating was wrinkled
Dioxolane (emulsion)	66.0	60.2	The coating was wrinkled
Benzyl alcohol	89.1	77.5	The coating was wrinkled
Diethoxyethane	120.8	108.7	The coating was wrinkled
Cyclohexanone ethylene ketal	32.2	30.0	The coating was wrinkled
Benzaldehyde ethylene acetal	66.5	56.4	The coating was wrinkled
Dipropoxyethane	60.0	54.0	The coating was wrinkled
Dibutoxyethane	58.8	54.7	The coating was wrinkled

## Brown plate

**Table 6.** Results of coating detachment study for the brown plate

Active ingredient	Force		Comments
	kPa	N	
-	507.4	456.6	A part of the coating was detached
N-methylpyrrolidone	754.5	679.0	The first layer of the coating was detached
Dimethoxymethane	-	-	The coating was wrinkled
Dioxolane (gel)	392.9	353.6	The coating was wrinkled
Dioxolane (emulsion)	169.0	152.1	The coating was wrinkled
Benzyl alcohol	8.3	7.4	The coating was wrinkled
Diethoxyethane	305.8	275.2	The coating was wrinkled
Cyclohexanone ethylene ketal	83.4	77.5	The coating was wrinkled
Benzaldehyde ethylene acetal	37.4	34.8	The coating was wrinkled
Dipropoxyethane	268.3	241.4	The coating was wrinkled
Dibutoxyethane	173.1	155.8	The coating was wrinkled

The same situation as in the green plate occurred in the case of the brown plate. We can see a decreasing force required to detach the coating, from 465 N for the reference sample, to 7.4 N for benzyl alcohol. The exception is a test in which the coating was treated with the preparation containing N-methylpyrrolidone. In this case, the coating was not wrinkled. However, it softened the coating, making it possible to remove all of the top layer.

Similar in this case, regardless of the partition coefficient, the substances caused wrinkling of the shell. As a result, the force required to detach the coating was reduced. The only exception is N-methylpyrrolidone. In its case, despite a low value of partition coefficient, it did not cause wrinkling of the shell.



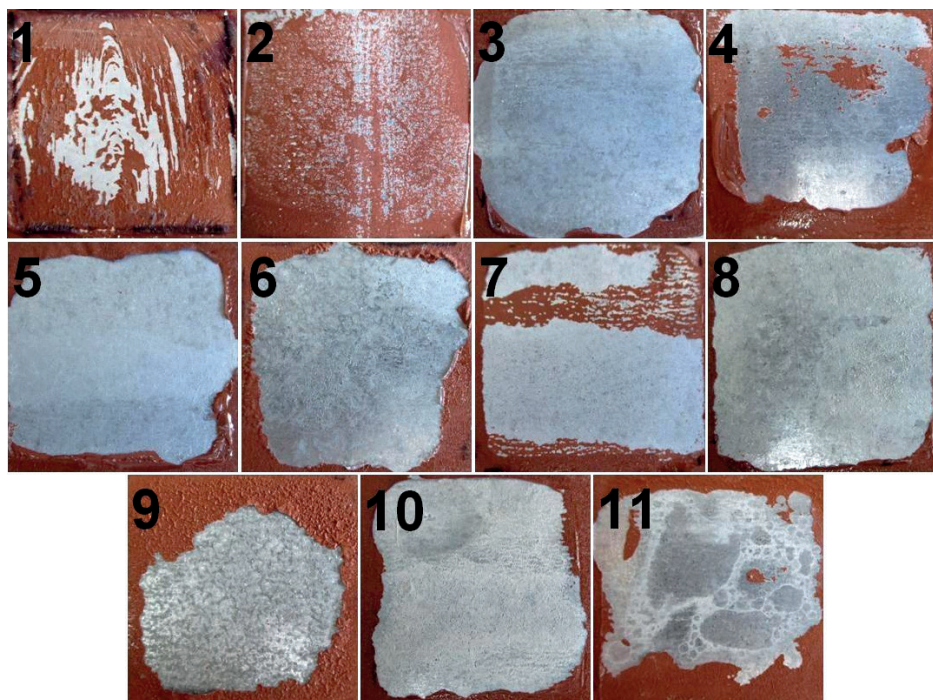


Fig. 4. The plate after study of coating detachment; 1 – reference sample, plate treated the preparation with 2 – N-methylpyrrolidone, 3 – dimethoxymethane 4 – dioxolane (gel), 5 – dioxolane (emulsion), 6 – benzyl alcohol 7 – diethoxyethane, 8 – cyclohexanone ethylene ketal, 9 – benzaldehyde ethylene acetal, 10 – dipropoxyethane, 11 – dibutoxyethane

## Epoxy plate

**Table 7.** Results of coating detachment study for the epoxy plate

Active ingredient	Force		Comments
	kPa	N	
–	650.7	605.1	A part of the coating was detached
N-methylpyrrolidone	194.6	181.0	A small part of the coating was detached
Dimethoxymethane	63.0	52.9	A part of the coating was detached
Dioxolane (gel)	249.6	224.6	A part of the coating was detached
Dioxolane (emulsion)	The coating was wrinkled		
Benzyl alcohol	The coating was wrinkled		
Diethoxyethane	599.9	521.9	A part of the coating was detached
Cyclohexanone ethylene ketal	249.3	224.2	A part of the coating was detached
Benzaldehyde ethylene acetal	506.2	439.4	A part of the coating was detached
Dipropoxyethane	411.0	369.9	A part of the coating was detached
Dibutoxyethane	204.9	190.6	A part of the coating was detached

In case of epoxy plate only dioxolane and benzyl alcohol caused wrinkling of the shell. In other cause substances caused softening of the shell. Thereby the force needed to detachment of the coating was less than in the case of coating didn't treat the preparation. In this case, we also can see that with increasing  $\log P$ , the ability to wrinkling of the shell is decreased. However, this is not as pronounced as in the case of acrylic coatings.

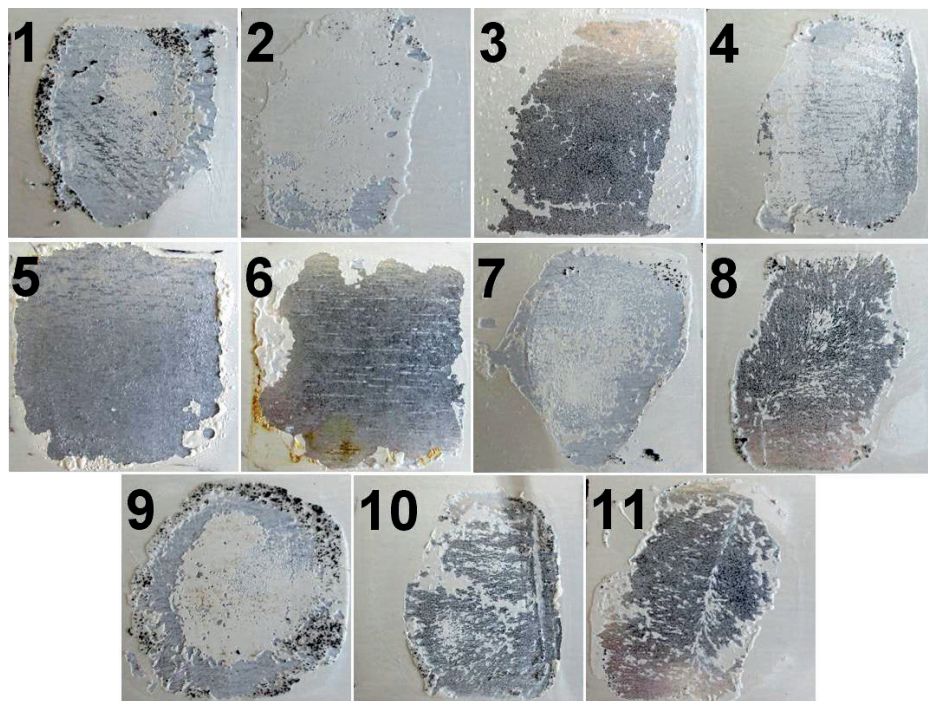


Fig. 5. The plate after study of coating detachment; 1 – reference sample, plate treated the preparation with 2 – N-methylpyrrolidone, 3 – dimethoxymethane 4 - dioxolane (gel), 5 – dioxolane (emulsion), 6 – benzyl alcohol 7 – diethoxyethane, 8 – cyclohexanone ethylene ketal, 9 – benzaldehyde ethylene acetal, 10 – dipropoxyethane, 11 – dibutoxyethane

#### 4. Conclusions

All the used active substances caused softening or wrinkling of the shell. The best results were obtained on plates painted with melamine-formaldehyde paint. In the case of the green and brown plates, most of the test substances caused wrinkling of the shell. Thereby, the force needed to detach the coating was significantly lower than in the case of the reference sample. The exception is N-methylpyrrolidone, which did not cause wrinkling of the shell in any of the cases. In the case of the plate with acrylic (blue and white) and epoxy coating, only dioxolane caused wrinkling of the shell. In the case of the blue plate, wrinkling of the shell was also caused by dimethoxymethane. In other cases, we observed softening of the coating. Additionally, we can see that, with an increase of the partition coefficient, the ability of wrinkling the shell is lower. The study shows that dioxolane and dimethoxymethane are the best substances to replace methylene chloride.

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