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**APPLICATION OF CENOSPHERE IN PASTES FOR  
CLEANSING HARD SURFACES****ZASTOSOWANIE MIKROSFERY JAKO PRODUKTU  
ODPADOWEGO W PASTACH DO CZYSZCZENIA  
TWARDYCH POWIERZCHNI****Abstract**

In the paper it was proved that commercial products: cenosphere and glycerin can be applied as valuable components of pastes for cleansing hard surfaces. In the pastes tested cenosphere was applied as abrasive, while glycerin as humectant. Cenosphere is a fraction of flying ashes obtained as a side product of coal combustion. The particles of cenosphere are ball-shaped. That is why they are more surface-friendly, as compared to other abrasives. Glycerin is a "waste" that is formed during synthesis of fatty acids methyl esters used to produce bio-diesel. Due to the large scale of bio-diesel fuel production, the quantity of glycerin obtained is huge – hard to dispose - causing its price decrease. Application of cenosphere and glycerin in pastes required new preparations and production technology, involving the components properties. Usable properties of the pastes obtained were comparable (or even better than) to commercial products. The pastes obtained are subject of a patent application.

*Keywords: pastes for cleansing hard surfaces, quality, cenosphere*

**Streszczenie**

W artykule udowodniono, że produkty handlowe, mikrosfera i gliceryna, mogą być pełnowartościowymi składnikami past do czyszczenia twardych powierzchni. W recepturach tych preparatów jako ścierniwo wykorzystano mikrosferę (Cenosphere), a jako humektant – glicerynę. Mikrosfera jest jedną z frakcji popiołów lotnych otrzymywanych jako produkt uboczny ze spalania węgla. Cząstki mikrosfery mają kształt kulisty i w większym stopniu niż inne ścierniwa ograniczają niszczenie czyszczonych powierzchni. Gliceryna jest „odpadem” powstającym podczas otrzymywania estrów metylowych kwasów tłuszczowych (FAME) wykorzystywanych do produkcji biopaliwa. Ze względu na skalę produkcji tego paliwa ilość powstającej gliceryny jest tak duża, że trudno ją zagospodarować, a dodatkowo jej cena spada. Zagospodarowanie mikrosfery i gliceryny w pastach wymagało opracowania nowych receptur i technologii wytwarzania, uwzględniając specyficzne właściwości tych składników. Właściwości użytkowe otrzymanych preparatów były porównywalne, a nawet korzystniejsze w odniesieniu do produktów handlowych. Otrzymane pasty są przedmiotem zgłoszenia patentowego.

*Słowa kluczowe: pasty do czyszczenia, jakość, mikrosfera*

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## 1. Introduction

The purpose of the research is to prepare cleaning pastes containing waste products (cenosphere and glycerin). Pastes for cleaning hard surfaces are one of the most popular groups of cleaners. They can be applied in cleaning gas and electric ovens, heavily soiled dishes, burnt pans, fume hoods, ceramic floor and wall tiles, stone tiles (granite, marble), PVC tiles, kitchen and bathroom fittings (e. g. steel covered with chrome), window frames and stills, balconies, tubs, sinks and other sanitary facilities. Such a wide range of applications requires proper adjustment of their content. These products should effectively remove dirt from various surfaces.

In the present work an attempt was made to show possible applications of cenosphere – the waste produced as a result of coal combustion in electric plants – as a modern abrasive in pastes for cleaning hard surfaces. Cenosphere has a specific structure – its particles are balls of diameter 10–500  $\mu\text{m}$ , filled with gas, for instance  $\text{CO}_2$ ,  $\text{N}_2$  (Fig. 1).

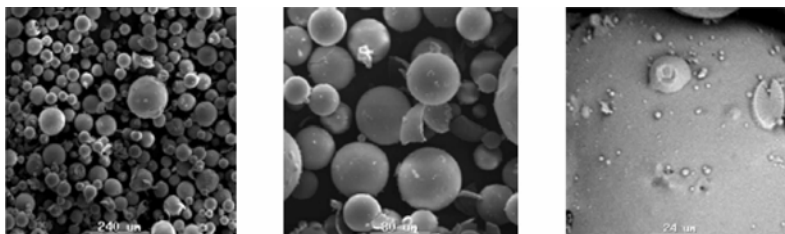


Fig. 1. Photographs of cenosphere balls made by scanning electromicroscope

Rys. 1. Zdjęcie kulek mikrosfery z elektronowego mikroskopu skaningowego

Due to the spherical shape of cenosphere grains it is predicted that they would not be so surface destructive as other abrasives. Moreover, high hardness (6–7 in 10-level Mosh scale) can improve their resistance, affecting cleaning process. These particles would not be then cracked and destroyed, resulting in lack of scratches on the surface cleaned. It was also observed that density of cenosphere is approx.  $0,4 \text{ g/cm}^3$  – this enables production of very efficient preparations [5–8].

Application of cenosphere in household chemistry products can gradually reduce its quantity in waste yards. It is predicted that cleaning pastes containing cenosphere as abrasive will reveal usable properties comparable (sometimes even better) to trade products [5–8].

In this paper the results of testing efficiency of cleaning various surfaces using cleaning pastes are presented. The results were compared to the properties of commercial products.

## 2. Characteristics of components of cleaning pastes

### Abrasive

*Cenosphere* – The cenosphere applied was obtained from flying ashes. It was cleaned and dried out. Its particles are balls 10–500  $\mu\text{m}$  in diameter, filled with gas.

**Humectant**

*Glycerin* – Technical glycerin produced by Centro-Chem, Poland was applied. It was supposed to prevent drying process in the pastes produced.

**Surfactants**

*Lauryl alcohol ethoxylate (m = 7)* – Lauryl alcohol ethoxylate ( $m = 7$ ) produced by PCC Rokita S.A. in Brzeg Dolny (Poland) was used.  $m = 7$  denotes the number of ethylene oxide moles per 1 mole of alcohol. It is a basic surfactant in cleaning pastes, responsible for cleaning and dispersion.

*C<sub>9</sub>-C<sub>11</sub> Pareth-6* – The mixture of alcohols C<sub>9</sub>-C<sub>11</sub> ethoxylated with 6 moles of ethylene oxide, produced by PCC Rokita, Brzeg Dolny, Poland, was applied. It is a nonionic surfactant responsible for cleaning and dispersion.

*Ethoxylate of rapeseed oil (m = 30)* – The product of Mexeo (Kędzierzyn-Koźle) was applied. Ethoxylates of rapeseed oil are solid wax substances, colour from yellow to brown, with characteristic smell. As nonionic surfactants they assist washing and are greasing agents.

**Sequestrant**

*Sodium citrate* – The product of Brenntag was applied. Sodium citrate by bonding multivalent metal ions is a sequestrant – enables removing mineral dirt.

**Viscosity modifier**

*Sodium carboxymethyl cellulose* – This is a colloid protector and thickener. It can form films and has good binding ability. It can be applied in household chemistry products (powders and cleaning pastes).

**Preservative**

*Euxyl 727* – a mixture containing phenoxyethanol, methylidibromo glutaronitrile, methylchloroisothiazolinone and methylisothiazolinone was applied.

**Perfume**

*Perfume "Orange"*, produced by Pollena-Aroma, Poland was used.

**Water**

Distilled water was used in production.

**3. Recipes for cleaning pastes**

On the basis of the literature data [1–2] and preliminary tests [9–10] three recipes for pastes for cleaning hard surfaces were designed [65]. In all the products the content of cenosphere was the same, equal to 60 wt.%. The pastes were diversified by the type and concentration of nonionic surfactants. The recipes for the pastes for cleaning hard surfaces are presented in Table 1.

Table 1

Recipes for cleaning pastes

| Compound                                 | PASTE  |        |        |
|--|--------|--------|--------|
|  | S1     | S2     | S3     |
| Cenosphere                               | 60     | 60     | 60     |
| Glycerin                                 | 7      | 7      | 7      |
| Lauryl alcohol ethoxylate<br>( $m = 7$ ) | 5      | 2.5    | 3      |
| C <sub>9</sub> -C <sub>11</sub> Pareth-6 |        | 2.5    |        |
| Rapeseed oil ethoxylate<br>( $m = 30$ )  |        |        | 2      |
| Sodium citrate                           | 2      | 2      | 2      |
| Sodium carboxymethyl<br>cellulose        | 0.26   | 0.26   | 0.26   |
| Preservative                             | q.s    | q.s    | q.s    |
| Perfume – “Orange”                       | 0.3    | 0.3    | 0.3    |
| Water                                    | to 100 | to 100 | to 100 |
| Colour                                   | q.s    | q.s    | q.s    |

Preparation of the cleaning pastes according to the recipes (Tab. 1) required a proper technology. It was crucial to solubilize carboxymethyl cellulose in a proper amount of water. In a separate mixer glycerin, nonionic surfactants, solubilized carboxymethyl cellulose, perfume and preservative had to be mixed. Afterwards, sodium citrate and cenosphere were introduced. The composition was mixed in a special mixer for 2 hrs, rotating speed 30 rpm, at 20°C.

After the pastes had been produced their stability was tested – stability of form, temperature, centrifugal and shaking were analyzed. The tests revealed that all the products had the desired stability.

The recipes for the pastes designed were compared to commercial products. From the range of available trade cleaning pastes four were selected and denoted randomly SH1, SH2, SH3 and SH4.

## 4. Experimental

### 4.1. Cleaning efficiency

The cleaning efficiency was assessed on the basis of ability to remove model dirt from ceramic surface. Ceramic plates 15 cm × 15 cm (surface roughness 0,36 µm) were cleaned and degreased with ethyl alcohol.

Next model soils were prepared. Two kinds of dirt were selected for testing: 1 – obtained from the norm PN-C77003 “Household chemistry products – washing up liquids – requirements and tests” and 2 – according to the test suggested by “IKW – Empfehlung zur Qualitätsbewertung der Produktleistung von Backofenreinigern” [12]. The soils were prepared right before the tests.

Dirt 1 was prepared by exact mixing the following components: 34 g of milk margarine, 34 g of flour, 20 g of powdered milk 70 g of egg yolk and 50 g of distilled water. Then,

12 g of the dirt (weighed with precision 0.01 g) was put on the plate and uniformly dispersed over the whole surface and left to dry out at room temperature (22°C). Additionally the following surfaces were cleaned: metal (steel, chromed and enameled), granite, marble and terrazzo.

Dirt 2 was obtained by mixing 20 g of sugar, 100 g of raspberry syrup and 20 g of flour. The whole mixture had been delicately warmed until the sugar was dissolved. On each plate 3.4 g of the composition was put and uniformly dispersed with a brush. The plates prepared in this way were then artificially aged in the incubator for 2 hours at 200°C. Finally the plates were removed and left at room temperature for 15 hours.

In order to clean the plates 2 g of the paste tested and 4 g of distilled water (weighed with precision 0.01 g) were placed on a sponge 5 cm × 8 cm × 2 cm. The sponge was applied to the ceramic plate and put under load of 1 kg. Afterwards 60 to-and-fro moves were made to imitate the cleaning process performed at households. Then the plate was rinsed with running water and dried out. The tests were performed at room temperature. The efficiency of cleaning was assessed visually according to the scale presented in Tab. 2. The procedure was repeated 3 times.

Table 2

**The point scale of cleaning efficiency**

| Number of points | Criteria  |
|------------------|---|
| 0                | No visible effect of the product on dirt  |
| 1                | Disarrangement of dirt structure; visible layer of dirt that was removed; slightly visible clearance of a white plate where the product was applied   |
| 2                | Disarrangement of dirt structure; visible layer of dirt that was removed; visible clearance of a white plate where the product was applied  |
| 3                | Disarrangement of dirt structure; visible (but faint) layer of dirt that was removed; visible clearance of a white plate where the product was applied or a wide area of dirt removed (diameter about 2 cm), not necessarily sharp; dirt was not removed completely |
| 4                | Serious disarrangement of dirt structure; sharp clearance of a white plate or a wide area of dirt removed (diameter about 2 cm); dirt was not removed completely  |
| 5                | Serious disarrangement of dirt structure; sharp clearance of a white plate or a wide and sharp area of dirt removed (diameter about 4 cm); dirt was not removed completely  |
| 6                | Dirt was completely removed in the area of product application  |

## 5. Results and discussion

### 5.1. Efficiency of removing dirt 1 by the original pastes (S1-S3) and commercial products (SH1-SH4)

An important parameter of cleaning products quality is their ability to remove dirt from various surfaces. The efficiency of cleaning using the pastes containing cenosphere and commercial products was assessed visually, according to the scale from Tab. 2. The results are shown in Fig. 2.

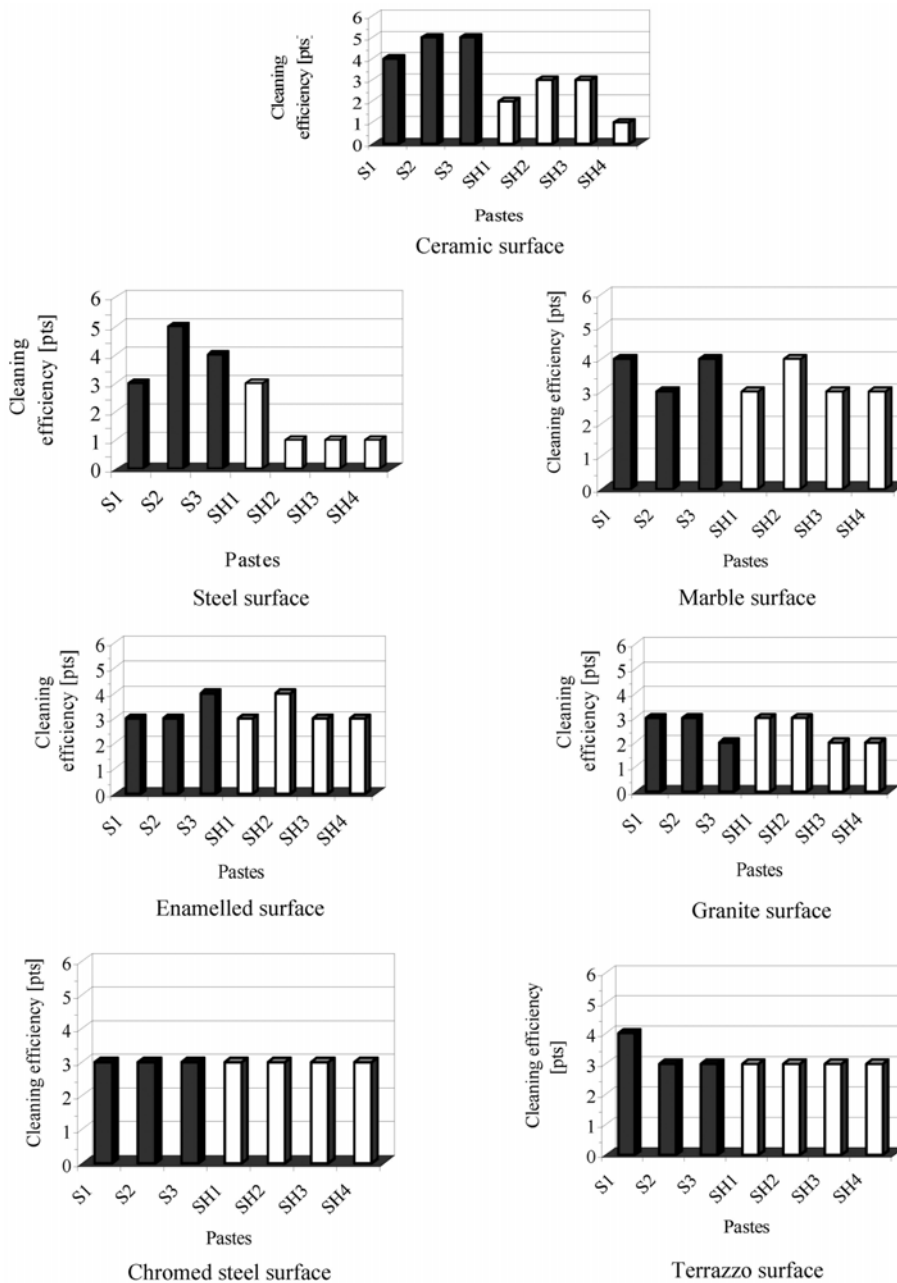


Fig. 2. Point assessment of ability to remove dirt from various surfaces (dirt 1) by the pastes tested

Rys. 2. Ocena punktowa zdolności usuwania zabrudzenia z różnych powierzchni (zabrudzenie I typu) przez badane pasty

On the basis of the test it was observed that the highest efficiency in removing dirt from ceramic surfaces (5 points) was revealed by two pastes containing cenosphere – S2 and S3. Slightly worse performance (4 points) was noted in the case of paste S1. The commercial products analyzed revealed significantly lower (1–3 points) ability to remove dirt from ceramic surfaces, as compared to the original products.

The highest efficiency in removing dirt from steel surface was observed for the paste containing the mixture of two nonionic surfactants: lauryl alcohol ethoxylate ( $m = 7$ ) and C<sub>9</sub>–C<sub>11</sub> Pareth-6, weight ratio 1:1 (S2). The two remaining pastes got 3 and 4 points. The most efficient commercial paste SH1 got 3 points, while SH2, SH3 and SH4 – 2 points each.

It can be concluded that in the case of the marble surface the products tested and the commercial product have similar efficiency of cleaning, belonging to the interval 3–4 points. Only one commercial product (SH2) and 2 original pastes (s1 and S2) got 4 points.

In the case of cleaning of the enamelled surface comparable efficiency of all the products was registered. The results are approximately 3–4 points.

The efficiency of removing dirt from the granite surface is comparable, equal to 2–3 points.

On the basis of the results one could observe the same efficiency of cleaning steel covered with chrome.

Also efficiency of terrazzo surface cleaning was tested. Paste S1 turned out to be the most efficient – 4 points. The remaining pastes revealed satisfactory performance and got 3 points.

#### 5.2. Efficiency of removing dirt 2 by the original pastes (S1-S3) and commercial products (SH1-SH4)

Also assessment of efficiency of removing dirt 2 by the pastes containing cenosphere (S1, S2 and S3) and commercial products (SH1, SH2, SH3 and SH4) was made according to the methodology introduced in “IKW – Empfehlung zur Qualitätsbewertung der Produktleistung von Backofenreinigern” [12]. The efficiency was assessed visually according to the point system presented in Tab. 3. The results are shown in Fig. 3.

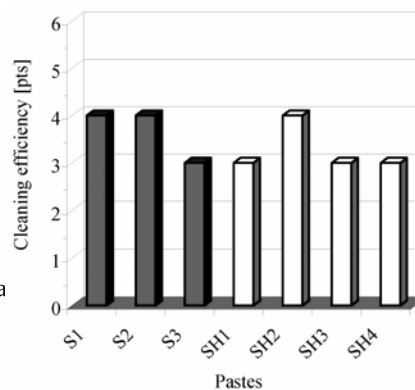


Fig. 3. Point assessment of ability to remove dirt 2 from ceramic surface by pastes S16, S35, S41 and SH1-SH4

Rys. 3. Ocena punktowa zdolności usuwania zabrudzenia z powierzchni ceramicznej (zabrudzenie II typu) przez badane pasty (S16, S35 i S41 oraz SH1-SH4)

The pastes were graded 3–4 points. Two original products (S1, S2) got 4 points, while only one commercial was awarded this note (SH2).

## 6. Conclusions

The results of testing ability to remove dirt by pastes containing cenosphere and glycerin are presented in the paper. Three recipes for cleaning pastes (S1, S2, S3) were designed. Their usable properties were verified and compared to commercial products (SH1, SH2, SH3, SH4). The ability to remove dirt 1 from various surfaces (ceramic, steel, marble, enamelled, granite, steel covered with chrome and terrazzo) and dirt 2 from ceramic surface was tested. Taking into consideration all the surfaces cleaned the commercial products were graded on average from 1 to 4 points, while the original ones (S1, S2, S3) – from 2 to 5.

The results presented prove that the pastes containing cenosphere and glycerin satisfy the criteria of cleaning agents. As far as efficiency is concerned these products are comparable (sometimes even better) than commercial products.

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