*Polish Journal of Chemical Technology, 11, **1**, 50 — 54, 2009, 10.2478/v10026-009-0012-3*

Preparations and production technologies of cleansing milks based on cenosphere obtained from flying ashes

Marian W. Sułek, Tomasz Wasilewski, Emilia Klimaszewska

Technical University of Radom, Department of Chemistry, ul. Chrobrego 27, 26-600 Radom, Poland, e-mail: twasilewski@pr.radom.pl

Application of cenosphere obtained from flying ashes as effective abrasive for cleansing milks was analyzed in the paper. Preparations and production technology of ten milks with various contents of cenosphere (from 2% to 20%) were designed. The products were tested to determine their most important usable properties. The efficiency of application and dispersion, cleansing ability, ability to emulsify fatty soils and destructing activity, measured as polish of surfaces, were analyzed. Selected trade products were tested analogously. The results obtained show that cenosphere can be a good replacement of abrasives that are widely used. The cenosphere-based products revealed comparable usable properties to the trade products (or even better). It is probable that producers of cleansers will pay their attention to this waste, which will bring profits to the natural environment.

Keywords: cenosphere, household products, scouring milk, quality.

INTRODUCTION

Cenosphere is a fraction of ash formed during combustion of coal. Its content in ashes is approximately between 0.6% and 2.5%. The structure of cenosphere is specific: its particles are balls with a typical diameter 10 μm – 500 μm, filled with gas, e. g. CO_2 or N_2. Most typical diameters belong to the interval 150 – 600 μm. The particle envelope consists mainly of oxides: silicon, aluminum, magnesium, iron, calcium and potassium. Cenosphere is dangerous to natural environment (can cause dustiness) due to its high volatility. That is why new possibilities of application cenosphere in economy are being researched[1 – 3].

Up to now cenosphere has been used as a filler of composite materials. It has been used with plastic and inorganic materials (e. g. concrete or water-glass). The low-density materials obtained in this way reveal good thermal isolation, low flammability and comparably low price. Owing to its application as a component of building and isolating materials cenosphere is produced on a commercial scale – thus reducing its price[1 – 3].

Analysis of powdered abrasives used in household chemistry products opens a possibility of an application cenosphere instead. At present materials like calcite, dolomite, marble calcium compounds and a number of polymers – polyethylene, polyvinyl chloride, polyurethane are used as abrasives. An important parameter characterizing these materials is their degree of fineness. Particles should have the size, shape and hardness that would allow removal of dirt mechanically, without destroying the surface being cleaned.

One of the most important parameters characterizing abrasives is the shape of particles. Particles having sharp edges can destroy the surfaces cleaned. Thus, common inorganic components should be ground to obtain proper granulation. The particles obtained in this way can, therefore have very irregular shapes[4 – 8].

In this research an attempt was made to show the possible applications of cenosphere as a modern abrasive in cleaning milks. A number of preparations diversified by its content were designed. The usable properties of these products will be assessed. Correlation of the results with the composition of the products will point out the optimal content of the abrasive tested in the cleaning milk. It will also allow designing its production technology.

EXPERIMENTAL

Components of scouring milks

For the production of scouring milks the following materials were used:

Cenosphere. Cenosphere plays the role of an abrasive. The microsphere applied was obtained from flying ashes. It was cleaned and dried. The fraction containing the molecules of diameters 10 μm – 500 μm was isolated from the product. Photographs of cenosphere balls made with the electron scanning microscope are presented in Fig.1.

Adduct of 7 moles of ethylene oxide to lauryl alcohol (Laureth-7). Rokanol L7 manufactured by Rokita (Brzeg Dolny, Poland) was used in the tests. Laureth-7 is the main sur-factant responsible for washing and dispersion.

Glycerine. A technical glycerine Centro-Chem (Poland) was used. The presence of glycerine in the products prevents its drying. It also is a moisturizer used in hands skin moisturizing cream.

Propylene Glycol. A pure propylene glycol manufactured by Merck was used. The presence of glycol in the products improves its cleaning efficiency.

Sodium citrate. The product of Brenntag was applied. Sodium citrate is a sequestrant – by binding the ions of polyvalent metals it makes removing of mineral dirt easier and in-creases the polish of the surfaces cleaned.

Acrylates / C10-30 Alkyl Acrylate Crosspolymer. The compound being a viscosity modifier (Carbopol 2020) was applied.

Preservative. The mixture of phenoxyethanol, methyl dibromoglutaronitrile, methyl chloroisothiazolinone and methyl isothiazolinone named Euxyl 727 was used.

Perfume. The composition "Orange" manufactured by Pollena-Aroma, Poland was applied.

Sodium hydroxide. The product of Brenntag is a pH-modifier.

Water. Distilled water was used for the preparation of the products.

Table 1. Composition of scouring milks

Components	Concentration [wt.%]									
	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Laureth-7	2	2	2	2	2	2	2	2	2	2
Glycerin	2	2	2	2	2	2	2	2	2	2
Propylene Glycol	5	5	5	5	5	5	5	5	5	5
Cenosphere	2	4	6	8	10	12	14	16	18	20
Sodium Citrate	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Preservative	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Perfume	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Aqua	Up to 100									
Sodium Hydroxide (20 wt.% aq.sol.)	Up to pH 8									

Recipes of cleaning milks

On the basis of the literature data and preliminary tests 10 recipes of milks with various cenosphere contents were prepared. Their composition is presented in Tab. 1. All the components, apart from cenosphere have constant concentrations.

The preparations were produced in the following way: sufficient quantity of water (temp. 23°C) was put into the main mixer. Then, the mixer arm was turned on (rotating speed 50 rpm). To the water Acrylates / C10-30 Alkyl Acrylate Crosspolymer was added gradually. The composition was mixed till a complete hydration of the polymer – about 4 hours. After that time, the remaining components were introduced, without any break of mixing. When the uniform consistence of the milk was reached, pH was regulated by an addition of the proper quantity of 20% solution of sodium hydroxide.

After preparation each product was tested for stability. Changes of look, dryability, resistance to temperature changes, fastness to centrifugal force and shaking were assessed. If no changes of the product structure had occurred after such a test the result was said to be positive. It turned out that all the preparations revealed required stability.

The results obtained for the milks containing cenosphere were compared with the ones obtained in the case of commercial products. Six commercial products (denoted H1-H6) were tested.

Methodology and equipment

The qualitative assessment of scouring milks is different due to the lack of literature data and the norms of proper research methodology. The methodology presented in the paper was prepared on the basis of experience and information contained in literature. It seems that the methodology described in this paper can be a foundation of objective assessment of cleansing products.

Assessment of application and dispersion efficiency

The efficiency of application and dispersion of the product over the surfaces cleaned was assessed in the following way. The ceramic plate 15 cm x 15 cm (roughness 0.36 μm) was prepared and gently cleaned in the water solution of the detergent. Moreover, the surface was degreased with ethyl alcohol. The plate was then placed vertically and attached to the base. Afterwards 4 g (with precision 0.01 g) of the milk was put on the clean and wet sponge 5 cm x 8 cm x 2 cm. The sponge surface was applied to the ceramic plate and moved circularly 5 times to widen the area cleaned as much as possible. Then the efficiency of application and dispersion were assessed due to the point system presented in Tab. 2. The procedure was repeated 3 times.

Table 2. The point scale of product application and dispersion efficiency

Number of points	Criteria
0	The preparation cannot be dispersed.
1	The preparation can be smeared over the surface, but most of it remains on the sponge.
2	The preparation uniformly covers the surface.

Assessment of action efficiency

The efficiency of action of the milks tested was assessed by the ability of the product to remove model dirt from the ceramic plate. The ceramic plates were prepared analogously to the ones used to assess the efficiency of application and dispersion. The model dirt contained 34 g of milk margarine, 34 g of flour, 20 g of powdered milk 7 g of egg yolk and 50 g of distilled water. The composition of the dirt was taken from the PN-C-77003 norm. The dirt was prepared every time right before the test.

On the surface of each plate 12 g of dirt was placed (weighed with 0.01 g precision) and uniformly dispersed. The dirty plates were placed in the incubator at 25° C for 24 hrs. to be dried out and fixed.

The plates prepared in this way were cleaned using a sponge 5 cm x 8 cm x 2 cm covered with 4 g of the milk tested and 2 g of distilled water (weighed with 0.01 g precision). The sponge was applied to the ceramic plate and put under the 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 according to the scale presented in Tab. 3. The procedure was repeated 3 times.

Assessment of ability to emulsify fatty soils

Testing the ability of emulsifying fatty soils by scouring milk was performed according to the methodology designed on the basis of PN-C-77003. The tests were performed in the following way: 1.7 or 1.8 g of rapeseed oil colored with Sudan red was rubbed with addition of the milk for 5 minutes. The mixture was then transferred into the 250 cm^3 measuring flask and filled up to the line. Afterwards the mixture was shaken for 5 minutes (the flask was rotated by 180°). The emulsion obtained in this way was placed in the incubator (45°C) for 30 minutes and assessed. The preparations were assessed according to the point system shown in Tab. 4. The observations were repeated 3 times.

Table 3. The point scale of cleaning efficiency

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

Table 4. The point classification of emulsions formed by the scouring milks

Number of points	Changes of emulsion look after 30 minutes at 45 ^{o}C
0	Clear drops or layer of oil in the flask neck.
1	Clear (more than 5 mm thick) fringe of emulsified oil in the flask neck.
2	Clear (3 to 5 mm thick) fringe of emulsified oil in the flask neck.
3	Clear (1 to 3 mm thick) fringe of emulsified oil in the flask neck.
4	Clear (less than 1 mm thick) fringe of emulsified oil in the flask neck.
5	Hardly visible fringe of emulsified oil in the flask neck, non-homogeneous bulk phase of the emu lsion (beginning of creaming).
6	No fringe in the flask neck, homogeneous emulsion.

Measurement of surface gloss after cleaning

Changes of plates polish after cleaning with the use of the products prepared were analyzed. Investigation of these changes before and after cleaning enables an assessment of the destructing effect of the products.

Cleansing the plates was run analogously as in the case of efficiency assessment, but no dirt was placed – the essence of the test was to show the action of the product on the material that the surfaces of the household equipment were made of. After cleaning the plates were rinsed in running water and dried.

A ZGM 1120 glossmeter produced by ZEHNTNER was employed for the assessment of surfaces polish. The apparatus directs at proper angle and intensity a light beam into the surface and measures the intensity of reflected light. The measurements were carried out for the 20º, 60º and 85º angles. The results are converted into proper values of gloss measured in GU units.

Both the roughness and polish tests were performed at room temperature in five random areas of the plate. Each measurement was repeated three times. The graphs show averaged values.

RESULTS AND DISCUSSION

Efficiency of application and dispersion over the surfaces cleaned

Efficiency of application and dispersion of the milks over the ceramic surfaces are presented in Tab. 5.

It was concluded that the content of microsphere does not affect the efficiency of application and dispersion over ceramic surfaces. The products containing 2 wt% – 16 wt% of cenosphere were graded 2 points. Above the 18wt% concentration of cenosphere the effi-ciency of application and dispersion was reduced to 1 point. All the commercial products were easy in application and dispersion – got 2 points.

The reduction in the efficiency of application and dispersion, which was observed in the case of milks containing the 18% and 20% cenosphere could be explained by their high viscosity. In the earlier tests of the same group of milks it was observed that the increase of the content of the abrasive (with the constant content of the remaining components) caused the increase of viscosity[9].

Efficiency of cleaning

The results of cleaning efficiency are presented in Tab. 6.

The efficiency of cleaning is one of the most important criterions of qualitative assessment of cleaning milks. During the cleaning process the solid particles contained in the product can disarrange the dirt structure and tear its parts from the surface. This has a direct effect on the speed and efficiency of removing dirt. In the case of the products with various contents of active cleaners this phenomenon is intensified with increasing the content of the abrasive.

In the case of milks containing 2, 4, 6, 8, 18 and 20% of cenosphere the cleaning efficiency was graded 3 points. The products containing 10, 12, 14 and 16% of the abrasive got 4 points. The results point out that the increase of cenosphere content improves their performance. On the other hand, very high content of the abrasive (18 and 20%) makes application and dispersion difficult (Tab. 5), resulting in a slight decrease of the cleaning efficiency.

Table 5. Efficiency of application and dispersion

Product	M1 2%	M2 4%	M3 6%	M4 8%	M5 10%	M6 12%	M7 14%	M8 16%	M9 18%	M10 20%	H1	H2	H3	H4	H5	H6
Efficiency of applic ation and di spersion [points]	2	2	2	2	2	2	2	2	1	1	2	2	2	2	2	2

Table 6. Cleaning efficiency

Product	M1 2%	M2 4%	M3 6%	M4 8%	M5 10%	M6 12%	M7 14%	M8 16%	M9 18%	M10 20%	H1	H2	H3	H4	H5	H6
Cleaning efficiency [points]	3	3	3	3	4	4	4	4	3	3	4	4	5	5	2	3

The analyzed commercial products revealed various activities in removing dirt. The grades belonged to the interval 2 – 5 points. These results show that the products containing cenosphere belong to the point interval observed for this usable property.

Ability to emulsify fatty soils

The results of the ability to emulsify fatty soils by the milks tested are shown in Fig. 2.

An important feature of cleaning milks is their ability to transfer fatty soils from the surface into the emulsion form. It prevents resettling of dirt on the surfaces cleaned. The results obtained (Fig. 2) point out that the increase of cenosphere content improves the fastness of the emulsions.

The preparations containing cenosphere got 2 to 5 points. The increase of cenosphere content resulted in improving the emulsifying ability. The results obtained for the commercial products were significantly diverse. Values from 1 to 5 points were observed. It is crucial that as many as 3 commercial products (H1, H3 and H4) got very low assessment of emulsification (1 – 2 points).

Destruction of the surfaces cleaned

In the tests analyzed up to now (efficiency of cleaning and ability to emulsify fatty soils) the presence of the abrasive in the product was profitable. In the case of the milks discussed one should not forget about the possibility of the destruction of the cleaned surfaces by the particles of the abrasive. In order to check the influence on the condition of the surfaces of the abrasive particles measurements of gloss were performed.

The gloss of the plate before cleaning was equal to 77 GU. After cleaning with the milks containing cenosphere no significant differences were observed. The values of gloss belonged to the interval from 76 to 81 GU. Similar values were registered after cleaning with commercial products. A slightly lower value was obtained for the product H3.

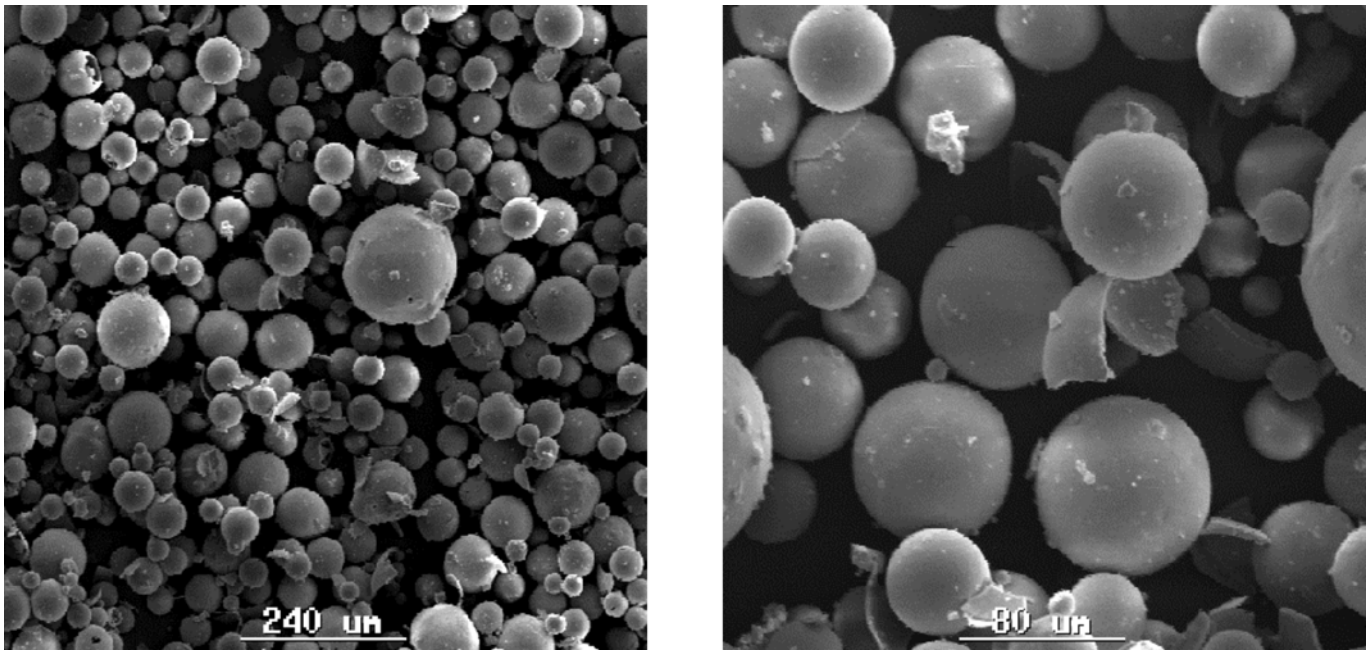

Figure 1. Photographs of cenosphere balls made with the electron scanning microscope

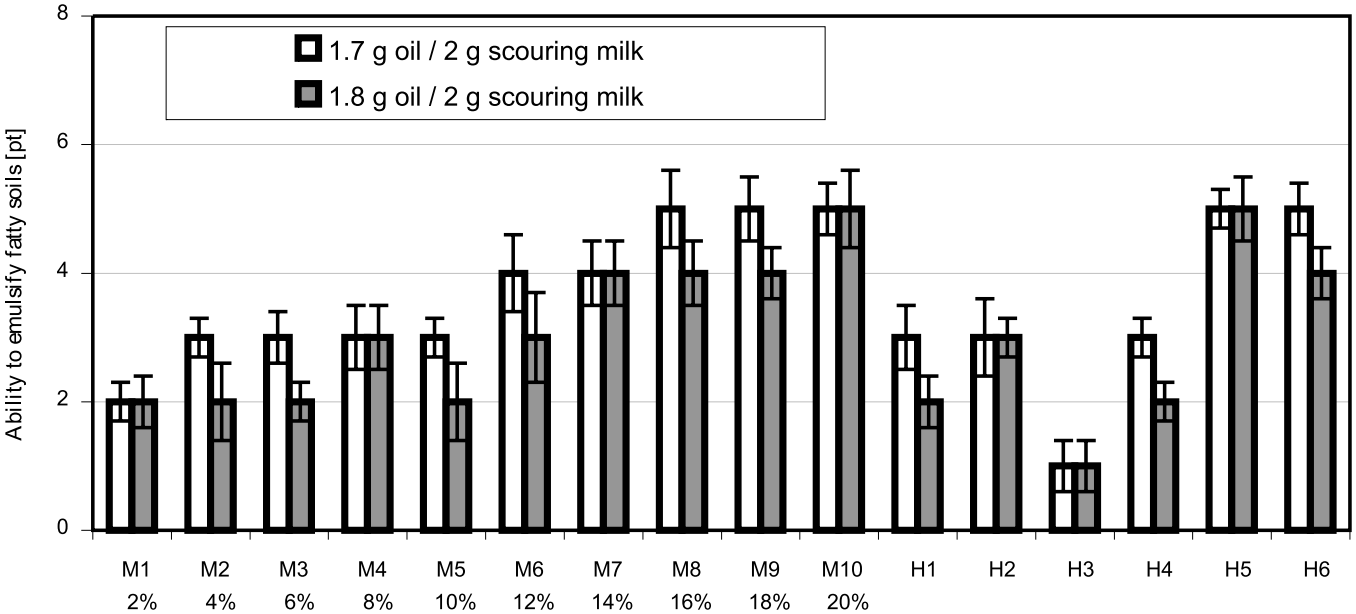

Figure 2. Ability to emulsify fatty soils

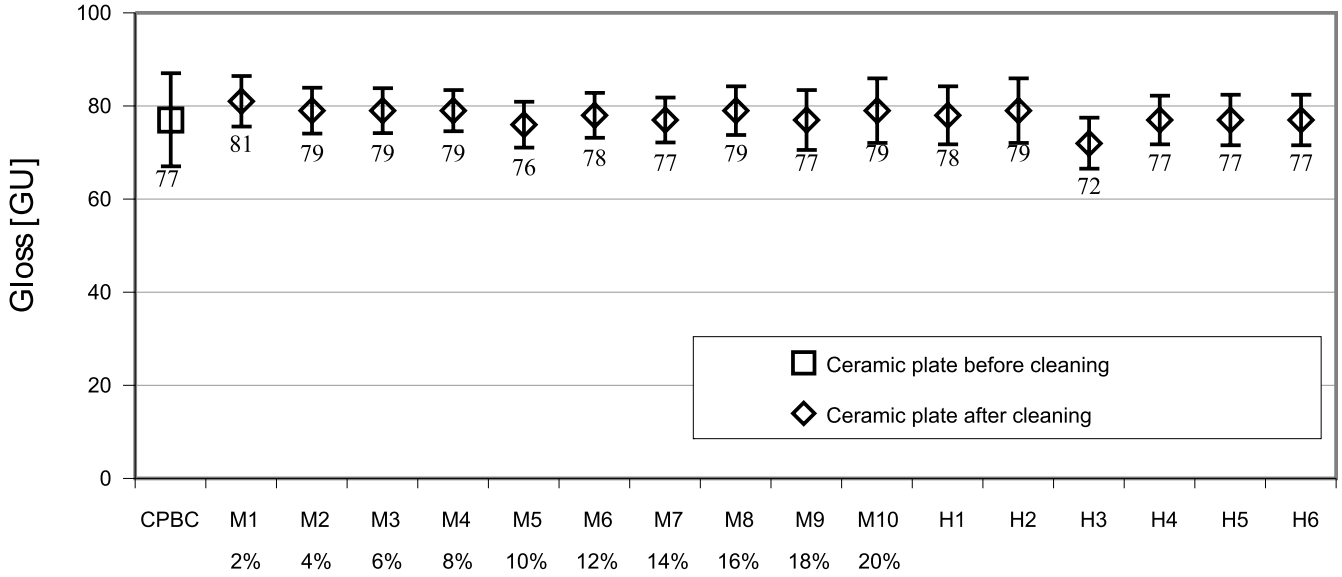

Figure 3. Gloss of ceramic plates after cleaning

The results obtained show clearly that application of cenosphere in cleaning milks does not worsen the gloss of the surfaces cleaned.

CONCLUSIONS

An attempt to design recipes of cleaning milks containing cenosphere was made in this research. The material is an abrasive. Most attention was paid to proper selection of the components to satisfy the most important qualitative criteria. The results obtained for the milks containing cenosphere were comparable to the selected commercial products.

The results can be a premise to the following conclusions:

– The cleaning milks containing cenosphere can be an alternative for the commonly used products with other abrasives;

– The increase of cenosphere content in milks improves the cleaning efficiency, emulsification of fats and softens the surfaces cleaned;

– The optimal cenosphere content can be estimated at 12 – 14%.

One can state that the goal of the research was achieved. The recipes and technologies as well as research methodologies described can be useful in the implementation of these new products. One can also expect that the application of cenosphere in cleaners can contribute to proper disposal of this hazardous waste.

Acknowledgements

This research has been financed by the State Committee for Scientific Research between 2006 and 2008, grant No R05 023 01.

The paper was written when the co-author – Tomasz Wasilewski – was a scholar of Foundation for Polish Science.

LITERATURE CITED

1. Pichor, W. & Petri, M. (2003), Properties of the cenospheres from coal ash, Ceramics 80, 705-710 (in Polish).

2. Technical brochure ZUTER S.A. (2008, July), from htpp://www.zuter.pl (in Polish).

3. Sulek, M.W., Wasilewski, T., Zieba, M. & Sas, W. (2007), The application of microsphere as abrasive in household chemistry products, *Polish Journal of Commodity Science* 3, 70 – 76.

4. Przondo, J. (2007), *Surfactants and their use in household products*, Ed. Technical Uni-versity of Radom, Radom, Poland, (in Polish).

5. Hauthal, H.G. & Wagner, G. (2004), *Household Cleaning, Care and Maintenance Products*, H.Ziolkowsky GmbH, Germany.

6. Lange, K.R. (1994), *Detergents and Cleaners*, CH Verlag, Germany.

7. Sulek, M.W., Wasilewski, T. & Pomagalska, M. (2004), Commodity science aspects of applications of alkyl polyglycosides in cosmetics and household products, *Commodity Science in accordance with integration with European Union*, Ed. Institute for Sustain-able Technologies, 625 – 629 (in Polish).

8. Arct, J. (1994), Washing, cleaning and scouring in household Part.3. *Drugstore News* 4, 25 – 27 (in Polish).

9. Sulek, M.W., Klimaszewska, E. & Pytlas, K. (2008), Selected Physicochemical Properties of Cream Cleaners of Strongly Contamined Surfaces as Characteristics of the Quality Assessment Products, *Polish Journal of Commodity Science* 1, 71-101 (in Polish).