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## THE APPLICATION OF HYDROPHOBIC CALENDULA OFFICINALIS FLOWER EXTRACT IN THE MANUFACTURE OF HANDWASHING LIQUID LAUNDRY DETERGENTS

**Abstract:** Liquid laundry detergents are aqueous solutions of surfactants and excipients. Currently, the market is witnessing a rapid development of products used in the washing process. This is mainly due to the constant competition of producers and constant changes in user preferences. Manufacturers, in order to meet the expectations of consumers increasingly introduce products of plant origin, which do not have a negative impact on both the user and the environment. The paper presents the results of research on the use of the marigold flower extract (*Calendula officinalis* Flower Extract) obtained under the conditions of supercritical carbon dioxide to produce handwashing laundry detergents. The substances included in this plant have a beneficial effect of bactericidal and soothing. The study analysed the impact of the concentration of the extract on the selected physicochemical and usable properties of washing liquids (stability, viscosity, turbidity, washing ability and foaming performance). It was found that with increasing concentration of the extract we can observe a decrease in viscosity and foam-forming ability. Furthermore, with increasing extract concentration, growth of turbidity occurs. There was no significant effect of the extract concentrations in hand washing liquid on their detergency.

**Keywords:** laundry detergent, quality, supercritical fluid extraction, plant extracts.

**JEL classification:** I20, E20, Q00.

## ZASTOSOWANIE HYDROFOBOWEGO EKSTRAKTU Z KWIATU NAGIETKA DO WYTWARZANIA PŁYNU DO PRANIA RĘCZNEGO

**Streszczenie:** Płyny do prania stanowią wodne roztwory związków powierzchniowo czynnych oraz substancji pomocniczych. Obecnie na rynku obserwuje się dynamiczny rozwój produktów stosowanych w procesie prania. Wynika to głównie z nieustannej konkurencji producentów oraz ciągłych zmian preferencji użytkowników. Wytwórcy, chcąc sprostać oczekiwaniom konsumentów coraz częściej wprowadzają na rynek produkty pochodzenia roślinnego, które nie wywierają negatywnego wpływu zarówno na użytkownika jak i środowisko naturalne. W artykule przedstawiono rezultaty badań dotyczące zastosowania ekstraktu z kwiatu nagietka (*Calendula Officinalis* Flower Extract) otrzymanego w warunkach nadkrytycznego ditlenku węgla do wytwarzania płynów do prania ręcznego. Substancje zawarte w tej roślinie wykazują korzystne działanie bakteriobójcze oraz łagodzące podrażnienia. W pracy analizowano wpływ stężenia ekstraktu na wybrane właściwości fizykochemiczne oraz użytkowe płynów do prania (stabilność, lepkość, mętność, pianotwórczość oraz zdolność piorąca). Stwierdzono, że wraz ze wzrostem stężenia ekstraktu obserwujemy spadek lepkości oraz zdolności pianotwórczej. Ponadto wraz ze wzrostem zawartości ekstraktu, następuje wzrost mętności preparatów. Nie stwierdzono natomiast znaczącego wpływu stężenia ekstraktu w płynach do prania ręcznego, na ich zdolność piorącą.

**Słowa kluczowe:** płyny do prania, jakość, ekstrakcja płynem nadkrytycznym, ekstrakty roślinne.

## Introduction

Laundry detergents are a group generating the highest revenues in the household chemicals industry (ca. 50% of total sales of household chemicals). Depending on the form, laundry detergents can be divided into solid and liquid types. Solid laundry detergents comprise powders, flakes and tablets. Traditional powder laundry detergents hold the largest share, both in terms of quantity (~80%) and value (~80%), in the laundry detergents market. Liquid laundry detergents include mainly liquids, gels and pastes designed for laundry purposes. Also worth mentioning are highly concentrated liquid laundry detergents enclosed in water-soluble capsules – an innovative form of laundry products which are becoming increasingly popular on the market. For a long time, the liquid form was applied solely in some special-purpose products such as liquid laundry detergents for washing delicates or wool fabrics. The development of liquid laundry detergents was a consequence of

introducing innovative technologies for obtaining new raw materials that could be successfully used in liquid formulations. Also, technologies for the manufacture of liquid laundry detergents are less cost-intensive (both at the stage of constructing a production plant and during manufacturing operations – low energy expenditures) in comparison with traditional technologies [Zieliński 2013; Przondo 2004; Smulders 2002; Boliński 1988; Hoffman and Kozłowski 1973; Yu, Zhao and Bayly 2008; Zhang *at al.* 2014; Scheibel 2004].

Laundry detergents in the form of liquids and gels are aqueous solutions of surface active agents and supplementary substances. They are responsible for surface wetting, washing baths penetration into the soil layer, soil swelling as well as solubilisation, emulsification and dispersion of soiling [Zieliński 2013; Przondo 2004]. The surfactants content ranges between 10% and 40%. The difference between gel and liquid laundry detergents lies in their viscosity. For liquid laundry detergents, it is typically in the range from 300 to 3,000 mPa·s. In contrast, the viscosity of gels is much higher, from ca. 6,000 even up to 20,000 mPa·s. Laundry detergents are based principally on anionic (Sodium Dodecylbenzenesulphonate, Sodium Laureth Sulphate, and alkaline soaps), nonionic (Laureth-7, Alkyl Polyglucosides, Cocamide DEA) and amphoteric surfactants (Cocamidopropyl Betaine). In addition to surface active agents, liquid laundry detergents also contain: enzymes, optical brighteners, viscosity modifiers, hydrotropes, antifoaming agents, antiredeposition agents, builders, dye transfer inhibitors, pH control, preservatives, dyes and perfumes [Yu, Zhao and Bayly 2008; Zhang *at al.* 2014; Scheibel 2004]. Laundry detergents in liquid form have a number of advantages including relatively low production costs, milder washing conditions than powders (ensuring better protection of colours and fabric fibres), ease of formulation with multiple ingredients and, in particular, the possibility of adding an extensive variety of surface active agents over a broad range of percentage quantities, complete and rapid dissolution in water, and more comfortable dosing [Smulders 2002; Boliński 1988; Hoffman and Kozłowski 1973].

Handwashing laundry detergents are in direct contact with the human skin of hands while the washing process takes place. Therefore, it is vital to ensure that detergents of this type not only demonstrate appropriate washing performance, but also have as little adverse effect on the skin of the hands (drying, irritation) as possible. An attractive solution is enriching detergent compositions with various types of hydrophobic plant extracts obtained in supercritical carbon dioxide conditions. Advantages of this method of acquiring raw materials include a relatively low temperature of extraction and absence of extractant residues in the finished product. Conducting the process

of extraction at a temperature close to 50°C makes it possible to preserve most active substances in extracts in a virtually unchanged form. It is an enormous benefit because when extracts are acquired using high-temperature steam distillation, a number of valuable compounds may be destroyed. For the purpose of the present study, it was assumed that enriching the composition of a laundry detergent with extracts of this type would reduce the adverse effect of the detergent's ingredients on the skin of the hands [Rój and Skowroński 2006; Rój and Skowroński 2006; Rój et al. 2009]. However, enriching the formulation with a hydrophobic extract requires the appropriate manufacturing technology and a preliminary analysis of the effects of the extract on the physicochemical and functional properties of finished handwashing liquid laundry detergents. Consequently, the present study seeks to define the effect of the *Calendula officinalis* flower extract obtained under supercritical carbon dioxide conditions on selected physicochemical and functional properties of handwashing liquid laundry detergents: stability, viscosity, turbidity, foaming performance and washing ability.

## 1. Materials and methods

### 1.1. Raw materials

As ingredients of handwash laundry detergents the following materials were used:

- *Sodium Laureth Sulfate*, Texapon N70 from Basf,
- *Sodium Dodecylbenzenesulfonate*, ABS Na paste from Brenntag Poland,
- *Laureth-7*, Rokanol L7 from PCC Exol SA,
- *Cocamide DEA*, Rokamid KAD from PCC Exol SA,
- *Cocamidopropyl Betaine*, Empigen BS/FA from Brenntag Poland,
- *PEG 40 Hydrogenated Castor Oil*, Emulsionante ELH 40 from Erca Poland,
- *Calendula Officinalis Flower Extract*, Extract obtained at supercritical conditions of CO<sub>2</sub> from the New Chemical Syntheses Institute, Supercritical Extraction Department in Pulawy, Poland,
- *Tetrasodium EDTA*, from Brenntag Poland,
- *Citric Acid*, from Brenntag Poland,
- *Methylchloroithiazolinone*, *Methylisothiazolinone*, Acticide MBS from Thor,
- *Sodium Chloride* from Brenntag Poland.

## 1.2. Methods

### Stability

In order to assess the stability of detergents, temperature tests were carried out. The tests allowed a visual assessment (colour, homogeneity, transparency) of detergents stored alternately at an increased (40°C, one day) and decreased (5°C, one day) temperature for a period of seven days. The reference point was that the product was not subjected to stability tests. The tests were performed in a CL-65 type incubator from ELKON and in an Amica refrigerator. On the completion of seven alternate cycles, the test samples were assessed visually.

### Viscosity

Dynamic viscosity was measured by a Brookfield PVS Rheometer. Measurements were taken at a temperature of 20°C and shear rate 10 s<sup>-1</sup>. The final result is the arithmetic mean calculated for three parallel tests.

### Turbidity

The Turbidimeter TN-100 Eutech Instrument was used for the research.

### Foaming abilities

The tests of the ability to form foam by the preparations were carried out according to the Polish Norm PN-EN 12728. Due to the method the foam is created by 100 ml of 1 % aqueous solution of the product tested. The foam is stirred in a glass cylinder for 60 s, making 60 hits. The ability to form foam was analysed as the volume of the foam formed registered 10 s after its creation. Additionally the per cent foam stability coefficient was evaluated as the ratio of the foam volume after 10 min. to the volume after 1 min.

### Washing ability

The washing ability of the tested liquid laundry detergents was determined on the basis of the PN-93/C-04810/01 standard. The method consists of the process of the washing of soiled test fabrics in specified conditions, in solutions of tested liquid laundry detergents and in a solution of a standard laundry detergent, followed by rinsing in water and drying, determination of the degree of lightness, and calculation of the washing ability. The tests were carried out with a white cotton fabric soiled by three types of soils: protein (hen eggs mixed in water), grease (cocoa mixed with sunflower oil) and dye (blackcurrant juice). The process of fabric washing was carried out according to the procedure described below. A 100 ml portion of a previously prepared

solution of a tested laundry detergent (10 g of the detergent was dissolved in 1L of water with a hardness of 4.28 mval/l) was transferred to a container. Next, two marked sections of a soiled cotton fabric (measuring 7 × 12 cm) and 10 steel beads were immersed in the solution. The procedure was repeated for every type of soiling. The container was closed and placed in a washing machine. The following conditions were adopted for the washing process: duration – 35 minutes, temperature – 40°C, rotational speed – 150 rpm. After completing the washing process the fabric was rinsed in water with a hardness of 4.28 mval/l. Following drying, the fabric samples were ironed, and their degree of whiteness was measured using a colorimeter. Three series of washing operations were conducted according to the above procedure. The mean of measurement results was used as a basis for calculating the parameters listed below:

- fabric washing ability (Y) according to the formula:

$$Y = \frac{X - B}{A - B} \cdot 100,$$

where:

X – mean degree of the whiteness of fabrics washed in a given laundry detergent,

A – mean degree of whiteness of a white unsoiled (control) cotton fabric,

B – mean degree of whiteness of white cotton fabrics soiled prior to washing;

- washing ability [%] of the tested laundry detergent for individual soiled types (X):

$$X = \frac{\overline{Y}_1}{\overline{Y}_2} \cdot 100,$$

where:

$\overline{Y}_1$  – mean fabric washing ability – for soiled fabric washed in the tested laundry detergent solution,

$\overline{Y}_2$  – mean fabric washing ability – for soiled fabric washed in the standard laundry detergent solution;

- final determination result (Z) [%] – arithmetic mean of the obtained washing ability results.

## 2. Results and discussion

Based on literature reports and the author's own experiences, model hand-washing liquid laundry detergents were formulated. The formulations contain surfactants of three types: anionic (Sodium Laureth Sulphate, Sodium Dodecylbenzenesulphonate), nonionic (Laureth-7, PEG 40 Hydrogenated Castor Oil and Cocamide DEA) and amphoteric (Cocamidopropyl Betaine). The formulations were additionally enriched with Tetrasodium EDTA (builder), Sodium Chloride (rheology modifier), Citric Acid (pH control) and a preservative. The formulations, as listed in table, differ in the content of the Calendula officinalis flower extract which was obtained in supercritical CO<sub>2</sub> conditions.

### Formulations of hand wash laundry detergents

Ingredients	Concentration [% w/w]			
	Rec. 1	Rec. 2	Rec. 3	Rec. 4
Sodium Laureth Sulfate	5.6			
Sodium Dodecylbenzenesulfonate	1.0			
Laureth-7	3.0			
Cocamide DEA	1.0			
Cocamidopropyl Betaine	0.9			
PEG 40 Hydrogenated Castor Oil	2.0			
Calendula Officinalis Flower Extract	–	0.1	0.3	0.5
Tetrasodium EDTA	0.2			
Sodium Chloride	3.0			
Citric Acid	q.s			
Methylchloroisothiazolinone and Methylisothiazolinone	0.2			
Aqua	do 100			

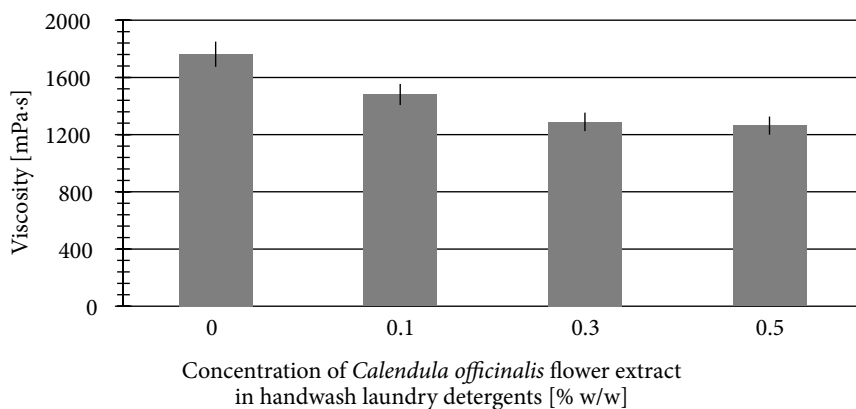
Producing the detergents in accordance with formulations (table) required the development of appropriate technologies. Sodium Laureth Sulphate, Sodium Dodecylbenzenesulphonate, 2% Laureth-7, Cocamide DEA and Cocamidopropyl Betaine were added to water. 1% Laureth-7 and PEG 40 Hydrogenated Castor Oil were separately combined with the extract by prolonged mixing until a homogeneous mass was achieved. Then, they were added to the aqueous solution of surfactants. At the end, a preservative, citric acid and sodium chloride were added.

To assess the stability of the tested detergents, temperature tests were carried out. Stability is one of the fundamental determinants of detergent

quality. No changes in the appearance of handwashing liquid laundry detergents were observed during their storage alternately at an increased (40°C, one day) and decreased (5°C, one day) temperature for a period of seven days. The reference point was that the product was not subjected to stability tests. All of the tested detergents demonstrated an appropriate level of stability.

## 2.1. Viscosity

The effect of the *Calendula officinalis* flower extract obtained in supercritical CO<sub>2</sub> conditions on the viscosity of handwashing liquid laundry detergents was assessed. The formulations of model liquid laundry detergents had the same concentration (3%) of the rheology modifier (sodium chloride).

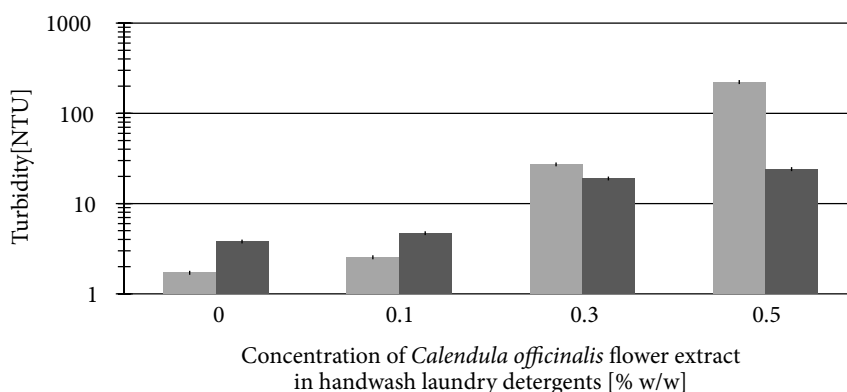


**Figure 1.** Effect of the concentration of *Calendula officinalis* flower extract on the viscosity of handwashing liquid laundry detergents. Brookfield PVS Rheometer, 10 s<sup>-1</sup>, 20°C

From the consumers point of view the viscosity is essential for the quality assessment. It determines the ability to wash and apply. It was found that with increasing concentration of the *Calendula officinalis* flower extract in handwashing liquid laundry detergents the viscosity decreases. The viscosity value of formulation without the extract was 1700 mPa·s. A 0.1% addition of the *Calendula officinalis* flower extract is accompanied by a ca. 16% drop in viscosity. A detergent containing 0.5% of the extract is characterized by the lowest viscosity. All handwashing liquid laundry detergents are characterized by sufficient viscosity for this kind of product.

## 2.2. Turbidity

To assess the clarity of the tested detergents, tests were performed with a turbidity meter. Turbidity is the opposite of clarity, expressed in NTU (Nephelometric Turbidity Units). Figure 2 presents the results of turbidity measurements of the tested hand washing liquid laundry detergents. The tests were performed for liquid detergents containing sodium chloride (3%) and not containing the *Calendula officinalis* flower extract.



**Figure 2. Effect of the concentration of *Calendula officinalis* flower extract and sodium chloride on the turbidity of handwashing liquid laundry detergents. Turbidimeter: TN-100 Eutech Instruments**

The content of the hydrophobic *Calendula officinalis* flower extract and sodium chloride was found to have a significant impact on the turbidity of the tested handwashing liquid laundry detergents. The turbidity of liquid laundry detergents rises along with an increase in the concentration of the extract. The turbidity of base detergents (without a viscosity modifier) varies between ca. 1.7 and 220 NTU. For comparison, distilled water has a turbidity of ca. 0.1 NTU. A significant increase in turbidity (222.3 NTU) can be observed for the liquid detergent containing 0.5% of the extract. It represents an increase in turbidity by ca. 220.6 NTU in relation to the liquid detergent which does not contain the extract.

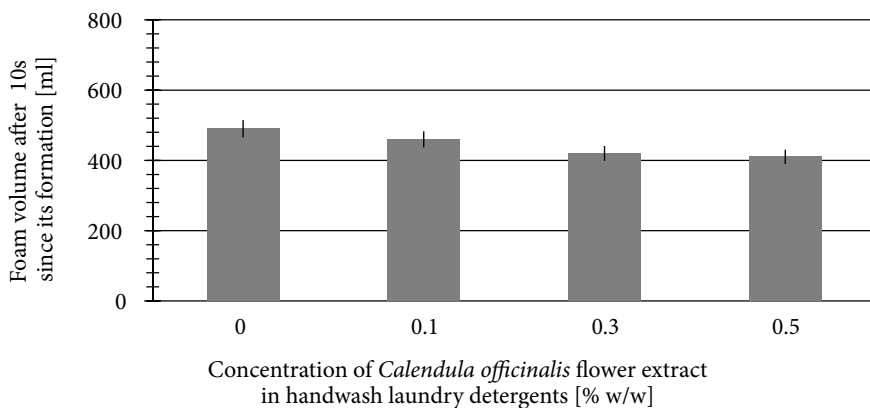
An addition of sodium chloride (3%) as a viscosity modifier leads to a change in the turbidity of tested handwashing liquid laundry detergents. The turbidity of the liquid detergents ranges from ca. 4 to 24 NTU. Sodium chloride (at appropriate concentrations) in aqueous surfactant solutions causes a change in the size and shape of micelles. Spherical micelles are transformed into cylindrical micelles which has an impact on the physicochemical

properties of the detergent, i.e. clarity and viscosity. However, when the system is enriched with a hydrophobic phase (e.g. a hydrophobic extract), sodium chloride can cause the formation of relatively large spherical multilayer aggregates in that system. Their presence induces an increase in the turbidity of the system, but at the same time causes a drop in the viscosity of the detergent.

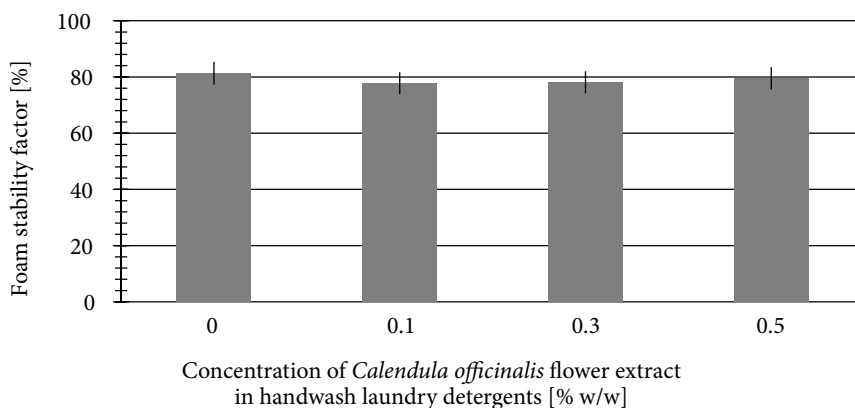
The increase in turbidity observed in a liquid laundry detergent not containing the *Calendula officinalis* flower extract (0%), and containing 0.1% of the extract, amounts to ca. 220% and 130%, respectively, compared to detergents not containing a viscosity modifier. Handwashing liquid laundry detergents containing 0.3% and 0.5% of the extract have a lower turbidity than base detergents (0% NaCl). The greatest difference was observed for the detergent containing 0.5% of the *Calendula officinalis* flower extract: the turbidity level decreased from 222.3 to 24.1 NTU.

### 2.3. Foaming abilities

Both in the process of automatic washing and handwashing, it is crucial that a laundry detergent has a relatively low foaming performance. Ample foam can cause problems, e.g. it may flow out of the washing machine or make it more difficult to rinse fabrics by hand. The foaming performance and foam stability index of the tested handwashing liquid laundry detergents were examined. The results are shown in Figure 3 and 4.



**Figure 3. Effect of the concentration of *Calendula officinalis* flower extract on the foaming abilities of handwashing liquid laundry detergent solutions**



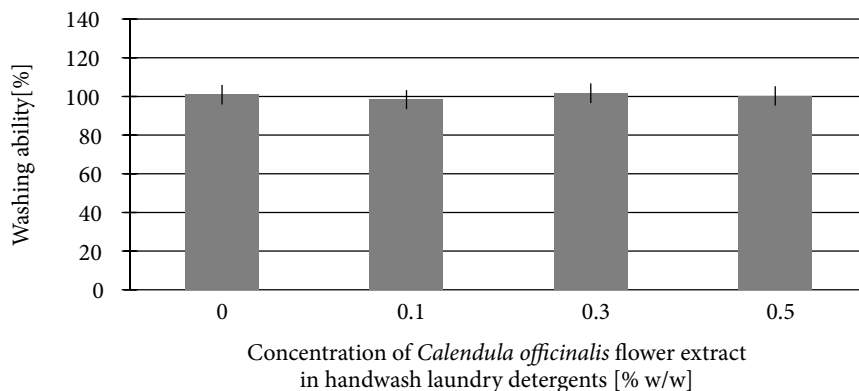
**Figure 4. Effect of the concentration of *Calendula officinalis* flower extract on the foam stability factor of handwashing liquid laundry detergent solutions**

The effect of adding the *Calendula officinalis* flower extract on the foaming abilities and foam stability factor of handwashing liquid laundry detergents was analysed. An increase in the concentration of the extract was found to reduce the foaming performance of the tested handwashing liquid laundry detergents. A base liquid detergent not containing the extract (0%) has a foaming performance of 500 ml. A 0.1% addition of the extract decreases the foaming performance by 30 ml. The foaming performance of liquid laundry detergents containing 0.3% and 0.5% of the extract is 420 ml and 410 ml, respectively. All of the tested liquid laundry detergents demonstrate a similar foam stability factor, ranging between 81% and 78%. Therefore, the hydrophobic *Calendula officinalis* flower extract added to liquid laundry detergent formulations can perform an additional beneficial function as an antifoaming additive.

## 2.4. Washing ability

Washing ability is the fundamental determinant of the quality of liquid laundry detergents. It needs to be stressed that the results of the assessment depend on various factors including the composition of the washing formulation, type of washed fabric, type of soiling, and washing conditions (e.g. water hardness, concentration and temperature of the washing water, duration and method of washing). In order to obtain comparable results of the assessment of washing ability, tests were performed on the basis of the Polish Standard PN-93/C-04810/01, applying the same parameters for all measurement cycles.

Figure 5 shows the washing ability of the tested liquid laundry detergents containing various amounts of the *Calendula officinalis* flower extract (0; 0.1; 0.3 and 0.5%).



**Figure 5. Effect of the concentration of *Calendula officinalis* flower extract on the washing ability of handwashing liquid laundry detergents**

The presented data shows that the washing ability of handwashing liquid laundry detergents remains at a similar level of around 100%. Consequently, enriching the formula with 0.1% of the *Calendula officinalis* flower extract does not cause significant changes in the washing ability of the tested liquid laundry detergents. Further increases in the concentration of the extract (up to 0.5%) in the liquid laundry detergents also failed to have any effect on the investigated parameter.

## Conclusions

The paper has presented the results of tests investigating the possibility of using the *Calendula officinalis* flower extract obtained in supercritical CO<sub>2</sub> conditions in handwashing liquid laundry detergents. The study analysed the concentration effect of the extract (0; 0.1; 0.3 and 0.5%) on selected parameters: viscosity, stability, turbidity, washing ability and foaming performance. Based on the test results, the following conclusions were made:

- The higher the concentration of the *Calendula officinalis* flower extract in handwashing liquid laundry detergents, the lower their viscosity.

- An increase in the extract concentration decreases the foaming abilities of the tested handwashing liquid laundry detergents. Consequently, the hydrophobic *Calendula officinalis* flower extract added to liquid laundry detergent formulations can perform an additional beneficial function as an antifoaming additive.
- The content of the hydrophobic *Calendula officinalis* flower extract and sodium chloride was found to have a significant impact on the turbidity of the tested handwashing liquid laundry detergents. The turbidity of liquid laundry detergents rises along with an increase in the extract concentration. In contrast, the addition of sodium chloride as a viscosity modifier leads to a change in the turbidity of the tested handwashing liquid laundry detergents. The greatest difference was observed for detergents containing 0.5% of the *Calendula officinalis* flower extract. The turbidity level was found to have decreased from ca. 222.3 (0% NaCl) to 24.1 NTU (3% NaCl).
- The concentration of the extract in handwashing liquid laundry detergents was not observed to have a significant effect on their washing ability.

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