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Emulsifier Effects on the Stability of Different Wax Emulsions

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Abstract
Wax emulsion has varied application in various industries. Wax and water are immiscible hence the choice of an effective emulsifier is key in formulating wax emulsions. This work focused on identifying an emulsifier as well as its adequate composition that would adequately give a stable wax emulsion. Paraffin wax emulsion was prepared by emulsifying different petroleum waxes (PW) in water using different emulsifiers namely Sorbitan monooleate (SPAN 80), Polyoxyethylene (20), Polysorbate 80 (TWEEN 80), Nonylphenol polyoxyethylene glycol ether (Rokafenol N6 and N22) together with ABS NaS. The relationship between the individual emulsifiers as well as a blend of two different emulsifiers and the multi – functional wax emulsion stability is established. Blends of SPAN 80/TWEEN 80 and Rokafenol N6/Rokafenol N22 are used. The two mixtures have a relatively similar effect on the stability of wax emulsion and hence the Rokafenol N6/Rokafenol N22 blend is further looked at. The most stable emulsion is formed from 2.5 wt% Rokafenol N6/Rokafenol N22 in a ratio of 80/20. Wax emulsion may be diluted with water to a ratio of 1:5 without loss of stability and changes in particle size.
Keywords: Wax emulsion, emulsifiers, hydrophobicity, Rokafenol N6, Rokafenol N22

1. Introduction

One of the main objectives of the oil industry is to deepen oil processing in order to obtain high-quality products that meet modern technical and ecological requirements. This desire has necessitated the modernization of existing and development of new processes of production of petroleum products, in particular is of great importance, on the basis of petroleum waxes (paraffin, petrolatum and slack wax) by the production of wax emulsions.

Wax emulsions are ubiquitous throughout nature and wide ranges of applications are found in the industry. Emulsion is a specific type of a colloid. A colloid is a mixture with one substance dispersed in the other at the microscopic level (Rattle, 2012).

Wax emulsion is a product, which is used to create superior protective properties of a material in a simple cost-effective manner. Easy application of emulsion without the need for heat and melting processes leads to the expansion of the range of applications in industry and in everyday life. For example, wax emulsions are used to impregnate paper and cardboard (Mujika-Farai *et. al.*, 2007), waterproofing wood-base materials (Mujika-Farai *et. al.*, 2007), waterproofing fabric fibers (Abo-Shosha *et. al.*, 2008), to create protective coatings of floors, car bodies and furniture, as well as the coating of fruits and vegetables (Thirupathi, Sasikala and John Kennedy, 2006; Kolattukudy, 1984)

The main advantages of wax emulsions compared to the traditionally used wax are that:

(a) The latter needs to be heated up to high temperatures before use; (b)Wax emulsions are simpler and more efficient to use; (c) No costs for storage (storage temperature of paraffin wax 5-30 ° C, and the molten wax is about 80 °C) (Rebinder, 1966). (d) No costs for transportation (in the case of the emulsion, it is not necessary to heat the pipes); (e) Fire safety (no risk of fire and injury of employees, which may occur when working with molten wax) (Rebinder, 1966; Rebinder, 1967).

One key component of wax emulsion formulation is the emulsifier that would serve as the emulsifying agent for the product. Wax and water would naturally not mix and hence an effective emulsifier is essential. This calls for the need of emulsifiers (surfactants) to stabilize the emulsion. Emulsifiers are a diverse group of chemicals, which vary structurally but mostly contain an oil–soluble hydrocarbon chain and a hydrophilic group which is water–soluble. They are surface–active substances which have the ability to be adsorbed at an oil–water interface and prevent the dispersed–phase droplets from aggregating in the emulsion. Selecting the emulsifier is also one key area that demands total attention in the producing of an emulsion (Anarjan and Tan, 2013).

Emulsifiers are surface-active substances whose molecules consist of a hydrophilic and a lipophilic part. A hydrophilic substance is a substance that has an affinity with water (Schaschke, 2014) and a lipophilic substance is a substance that has an affinity for lipids or promotes the dissolution of lipids. These properties bring the significance of the hydrophilic lipophilic balance (HLB) of emulsifiers that are critically looked at since it enhances the stability of the formed emulsion.

Hydrophilic-lipophilic balance (HLB) method established by Griffin (1954) was used to optimize compatible non-ionic surfactants for preparing stable emulsion (Schmidts *et al.*, 2010). Optimizing surfactant by using HLB number has been applied to almost all industries wherever surfactants are needed in product development, including food, cosmetic pharmaceutical, herbicide and pesticide formulation (Griffin, 1954; Han and Washington, 2005).

Different emulsifiers are used in the production of wax emulsions and this paper seeks to compare the effectiveness of using four different emulsifiers and comparing their effectiveness in giving the right stability as well as looking at the availability and cost effectiveness of using these emulsifiers.

2. Materials and Methods

Reagents used: Paraffin waxes (PW-1 was Paraffin NS, PW-2 was slack wax of Angarsk, PW-3 was slack wax of Omsk and PW-4 was petrolatum); Emulsifying agents (TWEEN 80, SPAN 80, Rokafenol N6, Rokafenol N22, ABS NaS), water.

2.1 Methodology

The content of petroleum wax in the emulsion was varied in the range of 20 - 50% (wt.), with the concentration of the emulsifier mixture ranging from 0.5 - 3.0% (wt.) and the water content from 50-70%.

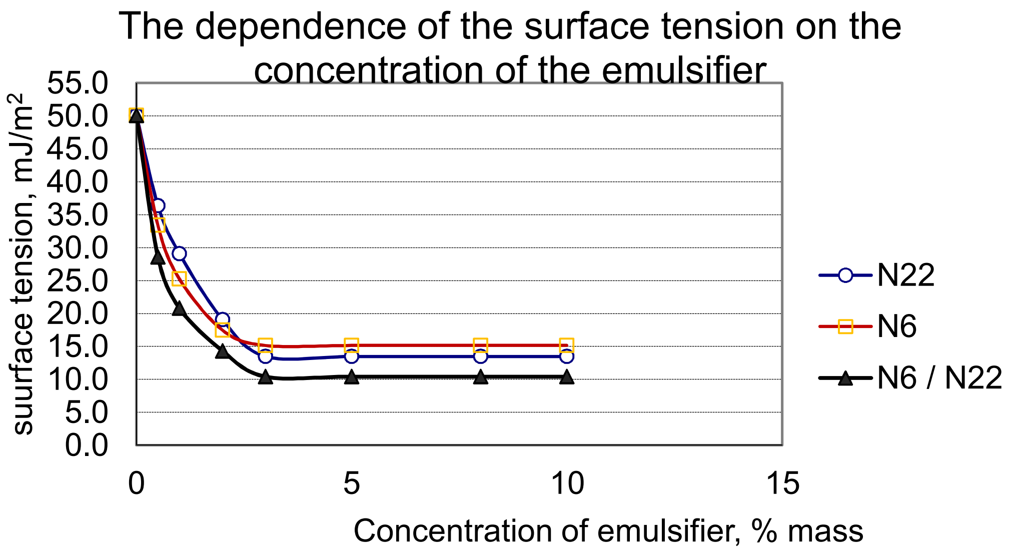
The process of preparing the wax emulsion was as follows:

- Mixing a predetermined amount of petroleum wax and an oil soluble emulsifying component (Rokafenol N-22, Rokafenol N6 and a blend as well as TWEEN 80, SPAN 80 and a blend) were mixed with constant stirring and heating to a temperature of 80 - 90 °C until a clear, homogeneous liquid was obtained;
- A predetermined amount of water-soluble component and an emulsifier (ABS NaS) were mixed with constant stirring and heated to a temperature of 80 - 90 °C until a transparent homogeneous liquid was obtained;
- Pre-heated mixture of wax and oil components of the emulsifying mixture was poured into another flask and agitated at 1000 rpm for 1 min;
- Pre-heated mixture of water and water-soluble components of the emulsifying mixture through a dosing device was fed batch wise into the flask containing the hot water at a stirring rate of 2000 rpm until a homogeneous milky liquid was obtained;
- Cooling the homogeneous liquid with cold water completed the emulsification process and the stirrer speed was reduced to 700 rpm. Cooling of the emulsion was carried out to a temperature of 30°C.

3. Results and Discussion

Typically, the value of the surface tension at the interface of two immiscible liquids is determined using a dropping pipette of Donnan. Because the experiment is carried out under standard conditions in which petroleum wax is in the solid state, this method is not suitable for determination in this case. Therefore, the value of the surface tension at the interface of petroleum wax (in liquid form after heating at a constant temperature) and the water was determined according to the rule of Antonov, whereby the surface tension at the liquid - liquid interface approximately equal to the difference between the surface tensions of mutually immiscible liquids at the interface with air.

Stable emulsion can be formulated with emulsifier or combination of emulsifiers, which compatible with required hydrophy-lipophyl balance (HLB) of oil phase used (Schmidts *et. al.*, 2010). A preliminary investigation on SPAN 80 and TWEEN 80 revealed that their use in the form of individual emulsifiers has considerable minimal stabilizing effect but their application in the form of mixtures give improved stabilizing effect. N6 and N22 emulsifiers were hence analyzed. The analyses confirmed that, both N6 and N22 gave a comparatively higher surface tension than the mixture. The higher the surface tension, the lower the stability. Figure 1 below shows the relationship between the emulsifier concentration and the surface tension with respect to emulsifiers N6 and N22 as well as a blend of the two.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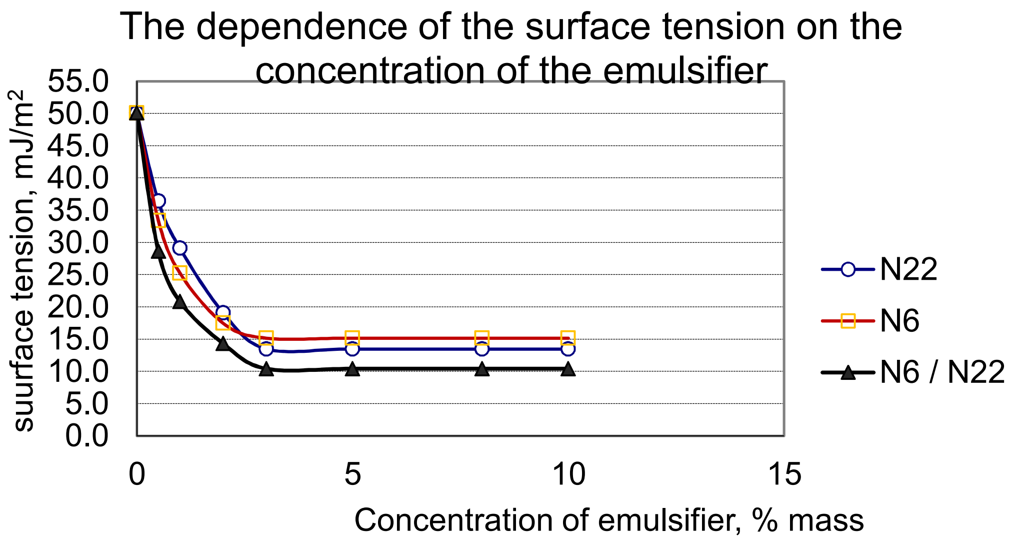
N6 / N22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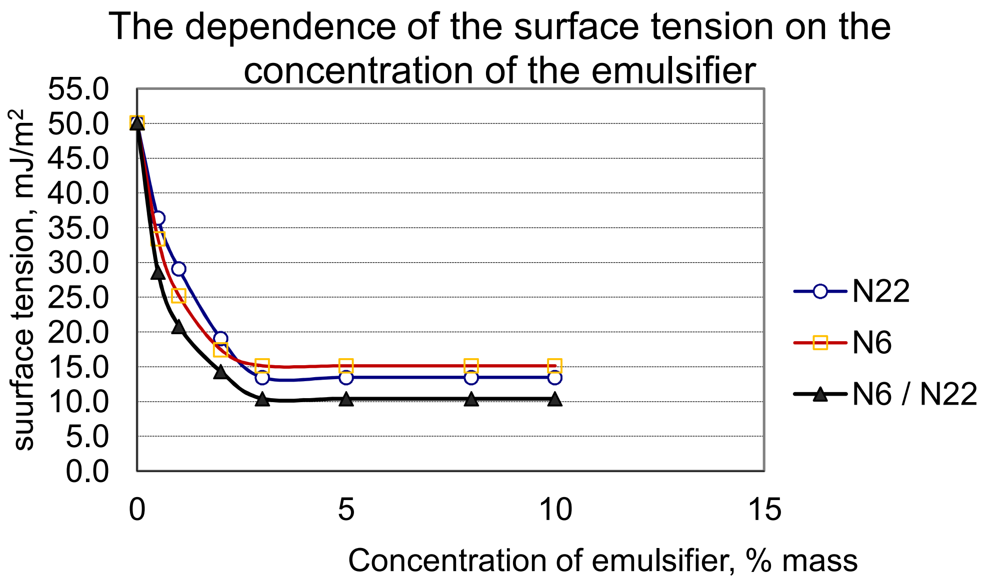
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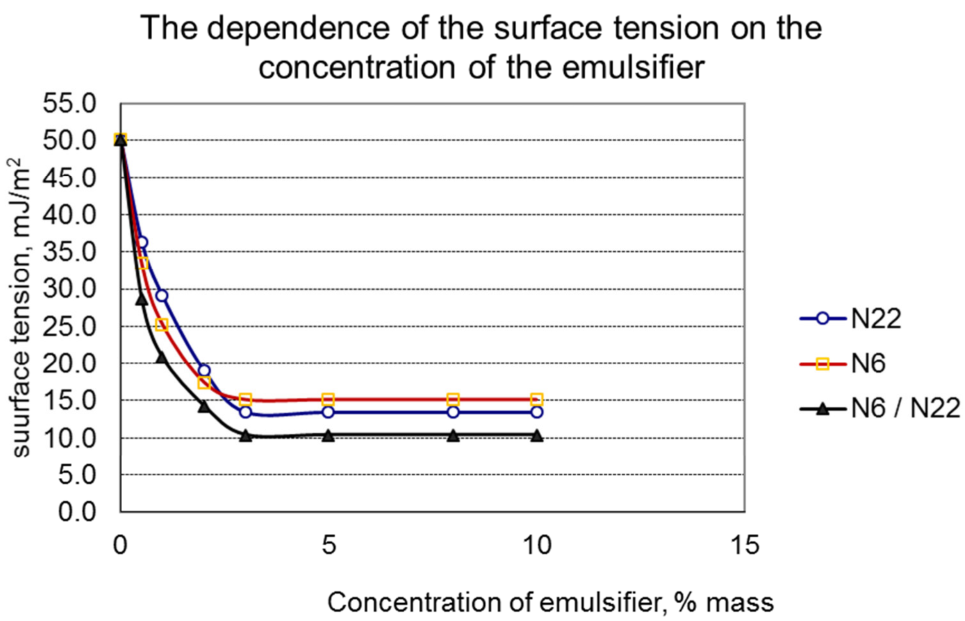
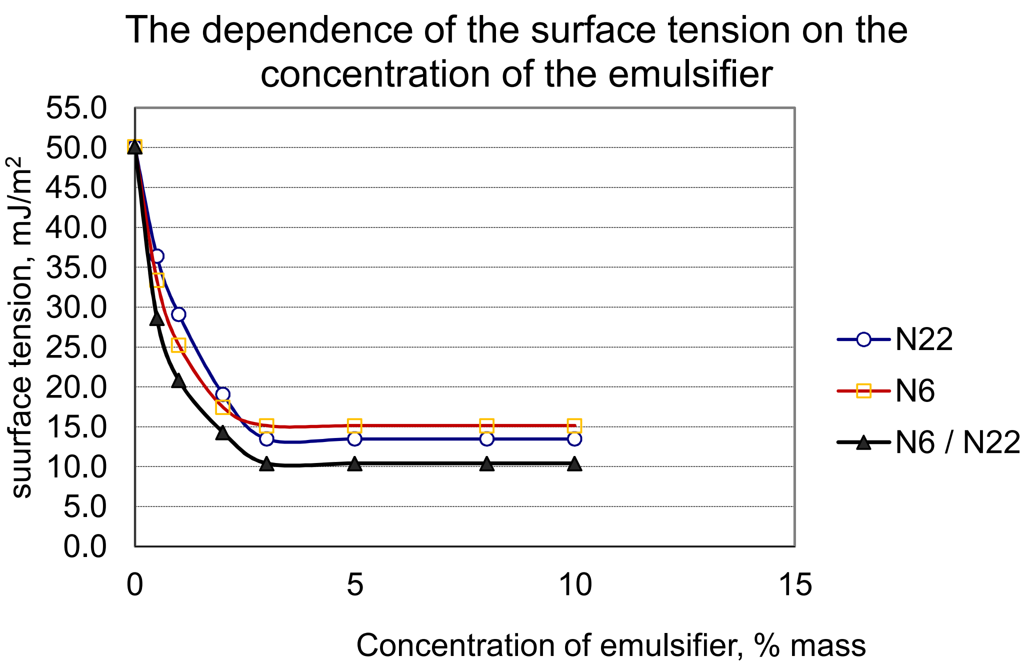


Figure 1: The dependence of the surface tension at the "petroleum wax - water" interface on the concentration of the emulsifiers N6, N22 and mixtures N6 / N22

A comparison between the mixtures of TWEEN 80/SPAN 80 and Rokafenol N6/N22 were looked at. The effectiveness of each emulsifier blend (Rokafenol N6 / N22 and TWEEN 80 / SPAN 80) in reducing the surface tension at the petroleum wax – water interface was analyzed. it was observed that by increasing the concentration of emulsifiers from 3% mass, the surface tension remains constant and, consequently, any further increase in the emulsifier quantity has no effect on the stability. Furthermore, although the mixture of emulsifiers SPAN 80 / TWEEN 80 has a better ability to reduce surface tension than mixtures N6 / N22, but this difference is not significant. The mixture of emulsifiers N6 / N22 is chosen for further studies based on availability of N6/N22 in the Russian Federation. The result of their performance is illustrated graphically in figure 2 below



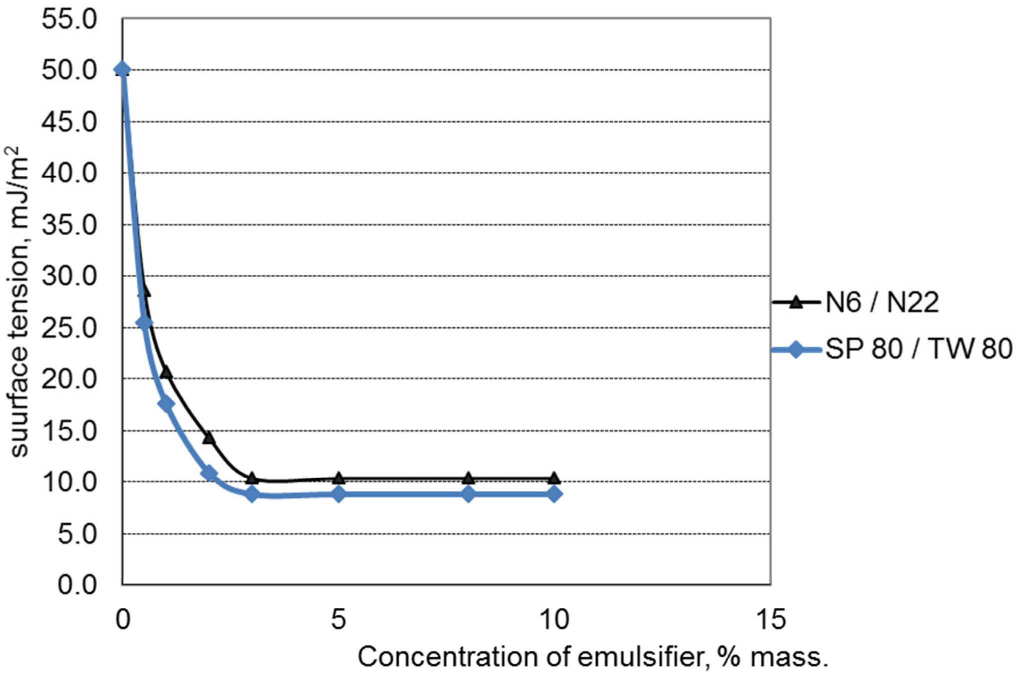


Figure 2: The dependence surface tension on the type and concentration of emulsifier

Effect of N6 / N22 emulsifier on the surface tension was also analyzed for all petroleum waxes (PW-1 - PW-4) used in the assay. For the four waxes analyzed it can be seen from the graph that the wax which has the highest surface tension is PW-4, which is petrolatum. Wax with the lowest surface tension was PW-1, while the other two waxes have a similar relationship. For mass concentration of 1% emulsifier, the surface tension for different waxes PW-1, PW-2, PW-3, PW-4 was obtained as 15.5; 14.6; 14.2 and 12.6 (mJ / m^2), respectively, and for the mass concentration of 5% emulsifier, the surface tension is 12.4; 11.8; 11.6; 10.8 (mJ / m^2) respectively.

An important quantitative characteristic of colloidal surfactants is the hydrophilic-lipophilic balance (HLB). The HLB is used to describe the colloidal properties of surfactants, which determines the relative efficiency of the hydrophilic properties of the polar group and the lipophilic properties of hydrocarbon radical of amphiphilic molecules (Griffin, 1954; Han and Washington, 2005).

For the relationship between the HLB and stability coefficient, K%, different mixtures of emulsifier were used on all four waxes analyzed in this experiment. Mixtures of different parts of 90/10, 80/20, 70/30 and 60/40 emulsifiers N6 / N22 were used to analyze waxes. HLB of emulsifier mixtures were 11.1; 11.6; 12.1 and 12.5 respectively. It can then be concluded that the highest stability was achieved with an HLB in the range of 11.4 - 11.8, which corresponds to the use of an emulsifier mixture in a ratio from 80/10 to 80/20.

Figure 3 shows the relationship between the surface tension at the petroleum wax – water interphase and the concentration of the emulsifier mixture whereas figure 4 gives an indication of the dependence of stability of the emulsion on the HLB of the emulsifier mixture.

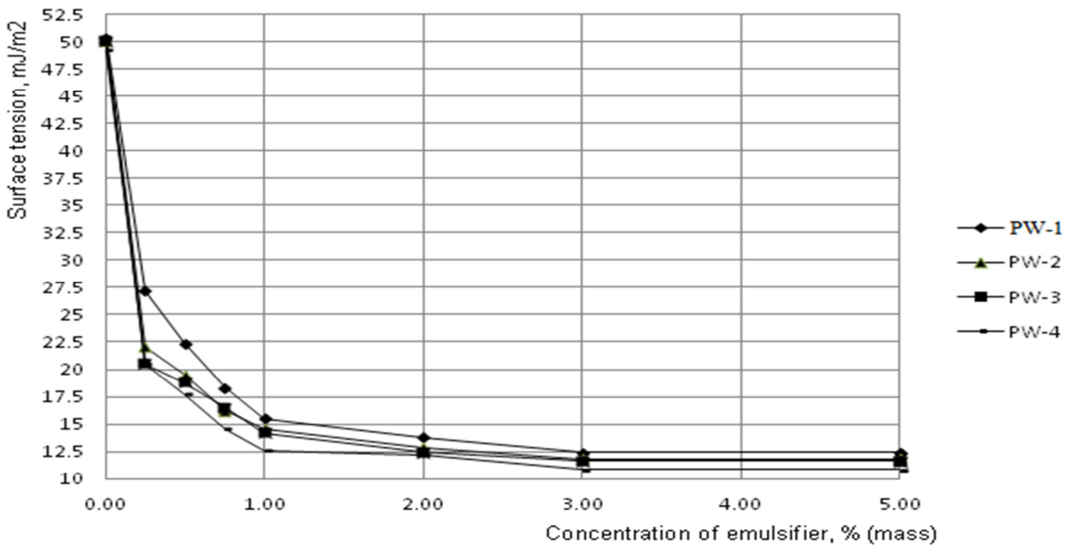


Figure 3: The dependence of the surface tension at the 'petroleum wax – water' interface on the concentration of the emulsifier N6/N22 for different waxes.

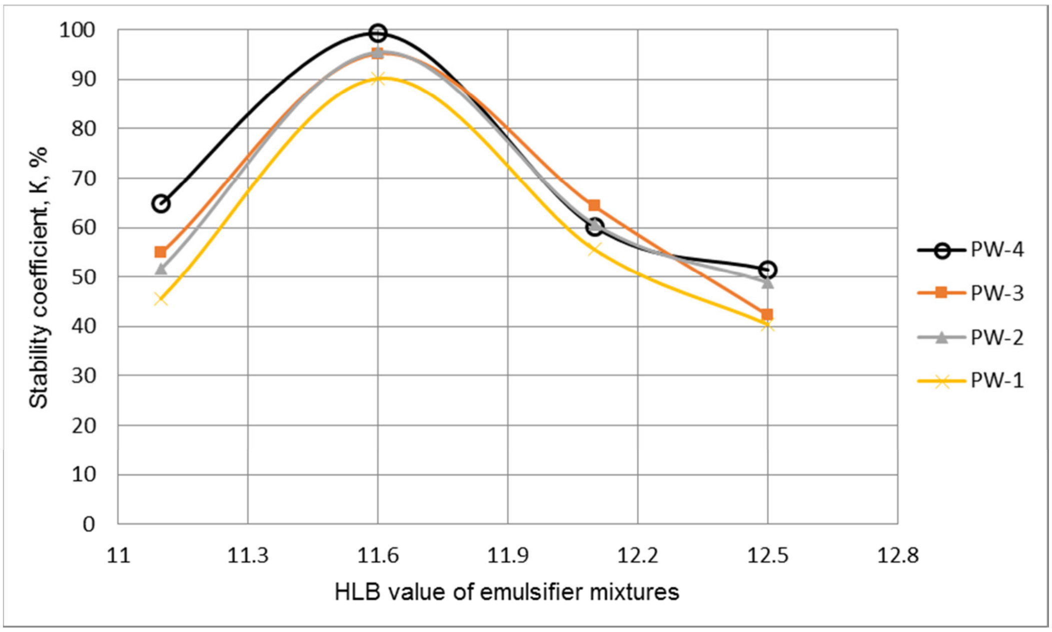


Figure 4: The dependence of the stability of the emulsion on HLB value of emulsifier mixtures N6 / N22 for the various petroleum waxes

Stability is one of the important indicators of emulsions, as characterized by a period of up to loss of basic properties. Loss of stability means not only a change in the basic quality indicators, but also the possibility of its use in industry for a long time. Table 1 presents data on the change of stability and particle size of the dispersed phase of the emulsions prepared based waxes PW-1 – PW-4.

Table 1. The stability of the wax emulsion by centrifugation and dilution

	Time to loss of stability of the emulsion, h	The amount of released water after centrifugation, %	Growth of the dispersed phase particle size, r %	Maximum dilution without loss of stability
Paraffin NS	460	16	18,1	1:2
Slack wax of Omsk	466	12	15,2	1:4
Slack wax of Angarsk	468	12	14,1	1:4
Petrolatum	472	10	10,4	1:5

To reduce the cost of transporting wax emulsions from the production site to the place of use, a concentrated formulation is prepared with the content of the dispersed phase (petroleum wax) being about 50 - 60% by weight of the emulsion. This should be easily diluted with water without precipitation of particles of wax or crust on the surface, and to be stable during storage, since in some plants such as fruits and cheese coating, about 3 - 5% wax emulsion is used. Especially important is the stability of the emulsions on dilution with water in their use in the home, for example in preparation of surfaces for subsequent painting. Concentrated wax emulsion in this case, after dilution with water are mixed by shaking the filled container, thereby increasing the tendency of the particles of petroleum wax to form agglomerates and lumps. Therefore, prepared wax emulsion containing a dispersed phase of 50% by weight and emulsifying the mixture in an amount of 2.5% by weight were diluted with water in the ratio of wax emulsion to water of 1: 2 to a ratio of 1: 5. The results of ultracentrifugation studies have shown that in all dilute emulsions the amount of released water phase does not exceed 15% of the total volume of the emulsion, indicating their high stability to dilution. When these dilute emulsions did not contain any sediment or particle agglomerates of petroleum waxes in the form of lumps, which was confirmed by measuring the particle size of the dispersed phase, which remained unchanged in relation to the concentrated emulsion. The findings of the emulsion after centrifugation and dilution are shown in Figure 5.

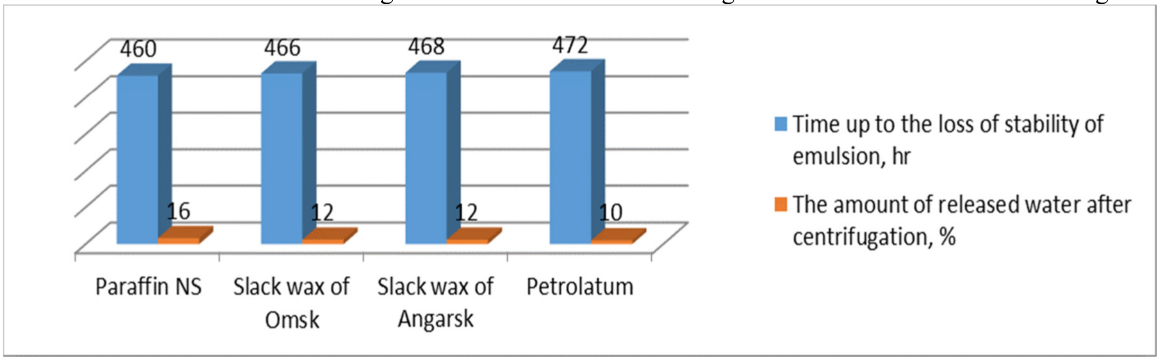


Figure 5: The stability of the wax emulsion after centrifugation and dilution

As seen from Figure 5, the most stable emulsions can be obtained based on wax PW-4 (petrolatum), the amount of released water after centrifugation was less than 10% and less stable emulsions were obtained from the wax PW-1 (paraffin NS) due to a high content of normal paraffins in its composition.

5. Conclusion

- The individual emulsifiers TWEEN 80, SPAN 80, Rokafenol N6 and Rokafenol N22 having HLB numbers as 4.3, 15.0, 10.8 and 15.0 respectively when used separately gave a less stable wax emulsion. Blend of TWEEN 80 and SPAN 80 as well as Rokafenol N6 and Rokafenol N22 gave more stable wax emulsion than the individual emulsifiers.
- The two blends gave a relatively similar wax emulsion stability with TWEEN 80/SPAN 80 being better but based on availability (in the Russian Federation at the time) of these emulsifiers, the Rokafenol emulsifiers were chosen over the TWEEN/SPAN since the difference in their performances was not so significant.
- Different proportions of the Rokafenol N6 and Rokafenol N22 were used to establish which blend gives the most adequate results required. The most efficient amount of the emulsifying mixture Rokafenol N6 /Rokafenol N22 was found to be 2.5% by weight (at a ratio of 80/20).
- Investigation of the physico-chemical and performance properties of the optimal composition of wax emulsions showed that wax emulsion may be diluted with water to a ratio of 1: 5 without loss of stability and changes in particle size;

Conflict of Interest

I wish to state that there is no issue of conflict of interest in relation to this work. It was purely an academic work.

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