Article

The Role of Preservatives and Multifunctionals on the Oxidation of Cosmetic O/W Emulsions

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Abstract: Preservatives are typically used to protect cosmetic products from microbial spoilage. However, there is evidence that some preservatives can increase oxidation in O/W emulsions. This could have disadvantages for product quality, efficacy, and consumer health and well-being. Therefore, the impact of preservatives or multifunctionals on oxidation should be quantified. For this purpose, five O/W emulsions with different preservatives were prepared and stored. During storage, the oxygen concentration in the headspace of the samples was studied. The samples showed significant differences in their oxygen uptake and daily oxygen consumption rate. Thus, the preservatives used in this study had an influence on oxidation.

1. Introduction

In recent years, synthetic preservatives such as parabens have fallen strongly into disrepute and have been dismissed by many consumers [1]. This is one possible factor for the steadily increasing demand for natural cosmetic products [2]. Although the type and concentration of preservatives are severely limited in natural cosmetic products, even in them substances have to be used to protect the products and consumers, especially in O/W emulsions.

O/W emulsions are dispersed systems composed of an outer water phase and a dispersed oil phase with emollients responsible for tactile perception and skin efficacy [3,4]. To prevent the separation of these non-mixable components, amphiphilic surface-active molecules—emulsifiers—are required [5]. An O/W emulsion is characterized by being water-soluble, cooling, and not oily. Despite the fact that emulsions are prone to flocculation, coalescence, or separation of the phases during storage [6,7], their quality can also be limited by the growth of microorganisms in the large water phase [8]. For example, bacteria, yeasts, and molds can enter the product after opening the packaging through contact with the finger, as well as exposure to air. Therefore, preservatives are used to prevent the growth of microorganisms [9]. In general, a preservative should have a broad spectrum of activity, sufficient solubility in water, and a pH-independent spectrum of activity, and should not interact with other ingredients [10]. Table 1 shows some selected natural preservatives, their respective pH range of action, water solubility, preservation spectrum, and the maximum permissible amount that may be used in the preparation of the various O/W-emulsion-based cosmetic formulations.

Table 1. Overview of selected preservatives.

Preservative	pH-Range	Water Solubility (g/L)	Preservation Spectrum	Max. Quantity [11] (%)
Phenethyl alcohol [12]	unlimited	20	gram −, mold	0.7–1.0
Potassium sorbate [13]	<6	582	yeast, mold	0.6
Ethanol [14]	all	unlimited	broad spectrum	20.0
Benzyl alcohol [15]	<4.5	40	broad spectrum	0.5
Glyceryl caprylate [16]	4.0–7.0	not specified	gram +, yeast	0.3–1.0

　　　While preservatives protect cosmetic products microbially, the bulk can still degrade due to oxidation. Oxidative changes in the lipid phase are mostly due to autoxidation processes of natural emollients. Like in most vegetable oils, these reactions are responsible for the formation of hydroperoxides and later carbonyl compounds, whereby the last mentioned can lead to a rancid off-flavor [17,18]. In particular, lipid hydroperoxides react with pro-oxidants from the aqueous phase to form radicals at the interface of the micelles, which subsequently trigger the oxidation of fatty acids inside the micelle [19]. The process of autoxidation is influenced by various factors, such as temperature, the composition of fatty acids, concentration and effectiveness of pro- and antioxidants, oxygen partial pressure, oxidation catalysts, such as heavy metal ions (e.g., copper, iron) and the redox-state [20]. The activity of the antioxidants decreases with lower the pH level, due to increased stability and solubility of the reduced transition metals responsible for pro-oxidant effects [21]. Some ingredients, such as citric acid, can form complexes with metal ions to prevent compounds from reacting with metals and forming peroxides [22], but others can even promote oxidation, as described for ascorbic acid [21]. It was already shown that the oxidation rate in O/W emulsions increases with the increasing content of unsaturated fatty acids [23]. However, the prediction of oxidation reactions in emulsions is not trivial due to numerous influencing factors, such as droplet size, interfaces, and oxidation kinetics [24]. During oxidation, degradation of the oxidation-sensitive unsaturated fatty acids occurs, which are known for their positive effect on the skin such as anti-inflammatory effect [25] or effect against atopic dermatitis [26,27]. The resulting oxidation products and free radicals have been shown to accelerate skin aging [28] and lead to skin damage [29,30]. The topical application of such oxidation products can damage the skin, especially the skin lubricant squalene [31,32]. Some food preservatives themselves tend to degrade tissues in the body faster than they rebuild and, therefore, can interfere with metabolism [33], which may be also possible for cosmetic preservatives and their effect on the skin. Besides natural oils and unsaturated fatty acids, also certain ingredients are sensitive to oxidation and can lose their effect during storage, such as ascorbic acid (vitamin C) [34], retinol (vitamin A1) [35], and ubiquinone (coenzyme Q10) [36]. Even if preservatives are not as much in the focus of the literature yet, there is evidence that some preservatives, while improving microbiological shelf life, can lead to altered oxidation of unsaturated fatty acids in the emulsion as well. In the following, five preservatives were examined in more detail: Phenethyl alcohol is a rose-scented substance that acts as a multifunctional on the one hand as a fragrance, but also as a fungicidal and bacteriostatic agent by inhibiting enzymes in bacteria and fungi [37,38]. It is photosensitive and can be synthetically oxidized to the corresponding aldehyde and further to acid [39]. This process has been described in organic synthesis in systems with two phases (organic and aqueous) [40], which suggests that it can be applied to O/W emulsions as well. Sorbic acid or its salts (sorbates) are currently used as an antimicrobial agent to prevent spoilage by mold, yeast, and fungi by interfering with various metabolic processes in the cell life cycle. Sorbic acid has a very high partition coefficient in the water phase, reaching microorganisms very well. However, it is oxidatively unstable in aqueous solutions depending on pH, the presence of other additives, and storage

conditions [41,42]. As a result of this degradation, carbonyl compounds are formed, which can lead to undesirable changes in quality and acceptability [43]. A plausible reason would be that the unsaturated carbon bonds are able to bind oxygen. Sorbic acid showed a significant pro-oxidant effect in foods [44,45]. These processes are probably also transferable to cosmetic O/W emulsions. Ethanol has a very good preservative effect with a broad pH action spectrum, which is due to its non-specific protein denaturation effect against all types of microorganisms [9]. Ethanol is able to oxidize to acetaldehyde and acetic acid [46]. However, this process has little relevance for cosmetic emulsions. Furthermore, there are data that exclude an influence on fat oxidation in oils [47]. Benzyl alcohol has a pleasant fragrance and is frequently used as a preservative [48,49]. However, it is oxidatively unstable. The substance oxidizes in the presence of oxygen in an aqueous solution to benzaldehyde and further to benzoic acid, which acts against microorganisms [50,51]. Its bacteriostatic and fungistatic activity is based on the inhibitory effect on enzymes that degrade reactive oxygen species [52]. Benzoin derivatives can be problematic because they can react to carcinogenic benzene in the presence of hydroxyl radicals (e.g., from fat oxidation) and light [53,54]. Since these processes have already been described in foods [55], they are certainly also realistic in cosmetic emulsions. Glyceryl caprylate is known as multifunctional and acts as a natural preservative, but also as an emollient, emulsifier, and skin penetration enhancer [56,57]. The substance has a good effect on numerous bacteria, yeasts, and molds [58,59]. No evidence of pro-oxidant behavior could be found. This is due to the chemical structure, which does not contain any unsaturated bonds or free functional groups that preferentially undergo radical or oxidative reactions. This can also be assumed for emulsions. These data suggest an influence of preservatives and multifunctionals on the oxidation of emulsions. However, according to the knowledge of the authors, no study was found in the literature that systematically describes the effect of preservatives on the oxidation of emulsions. Therefore, there is a need to elaborate on this aspect with a comparable and reproducible experimental approach.

For that reason, the aim of the study was to determine the role of these substances on the oxygen uptake and daily oxygen consumption rate of cosmetic formulations. For this purpose, O/W emulsions were chosen as matrices for incorporating the substances and measuring oxidation. These results can help to select preservatives and multifunctionals that avoid pro-oxidant effects in the future so that oxidation and its negative consequences on the quality in terms of efficacy of the products, skin health, and consumer acceptance and well-being can be prevented.

2. Materials and Methods

To verify this effect, five formulations were prepared with the following natural preservatives: phenethyl alcohol, potassium sorbate, ethanol, benzyl alcohol, and glyceryl caprylate. It was not possible to prepare a blank value without preservatives, since the microbiological activity would have influenced the oxygen concentration in the headspace and prevented conclusions about oxidation. A method to sterilize the samples without significantly altering them, and thus, risking comparability was not known. For every preservative, one formulation was produced. The following ingredients were used: canola oil as emollient, glyceryl stearate SE as O/W emulsifier, xanthan gum as a stabilizer, pH regulator, and preservative. Double-distilled water was added to fill the difference to 100% since it was assumed, that the preservatives accumulate in the water phase due to their polar solubility and antimicrobial effect in the aqueous phase. The process involved suspending the thickener and emulsifier in the lipid phase and then homogenizing with the water phase heated to 80 °C at 17,000 rpm for one minute. After cooling while stirring, the pH was adjusted to 4.3, and the preservative was added by homogenizing at 17,000 rpm for one minute. Table 2 shows the formulations in detail.

Table 2. Overview of the formulations used.

Preservative	Water (%)	Canola Oil (%)	Glyceryl Stearate SE (%)	Xanthan Gum (%)	pH-Regulator (%)	Preservative (%)
Phenethyl alcohol	69.3	22.8	7.0	0.2	0.2	0.7
Potassium sorbate	69.8	22.8	7.0	0.2	0.2	0.2
Ethanol	55.0	22.8	7.0	0.2	0.2	15.0
Benzyl alcohol	69.5	22.8	7.0	0.2	0.2	0.5
Glyceryl caprylate	69.7	22.8	7.0	0.2	0.2	0.3

The samples were filled into vials with oxygen sensors as triplicate determinations and evacuated to 300 mbar for 30 s to remove air bubbles from the sample caused by the filling process. Next, the samples were sealed gas-tight. All these steps were performed in a sterile bank and allowed the most hygienic production possible. Subsequently, the products were stored for 96 days under accelerated conditions at 30 °C and commercial lightning (1000 lux, halogen, 6000 K). Light exposure was chosen since it leads to a higher oxygen uptake [60]. Since cosmetic products are, these conditions are transferable to practice. Cosmetic formulations are often developed for a storage period of 30 months, during which they are stored under illumination in the retail trade during the day in an often light-transmitting packaging. Therefore, using the Arrhenius equation, the storage chosen in this study might represent the first 5–6 months after production. Physical stability was assessed visually during the storage period, as previous rheological studies during product development and the recommendations of the ingredient manufacturers have shown stable formulations. The antimicrobial efficacy of preservatives in the used concentration ranges has already been approved by the ingredient manufacturers as well. These results could be applied to these applications. Microbial analysis was performed at the beginning of the storage. Individual microbiological challenge tests were not necessary here, since no additional microbial contamination or growth was expected due to the closed storage. After storage, all vials were analyzed using headspace gas analysis on their CO_2 concentration as a marker for microbial activity [61]. The experimental measurement of the oxygen partial pressure of the headspace was carried out via chemical–optical sensors according to the literature [62,63]. The oxygen concentration in mbar in every vial with a defined weight of product was converted to the amount of oxygen in mg taken up by 100 g of product (oxygen uptake) and shown as a function of time for all developed formulations to visualize the oxygen sensitivity. Subsequently, the slope of the oxygen uptake over time was calculated into the oxygen intake in mg per 100 g of product per day of storage (oxygen consumption rate) and is shown as a bar chart as an indicator of the oxidation kinetics [64]. The experimental setup is shown in the following scheme (Figure 1).
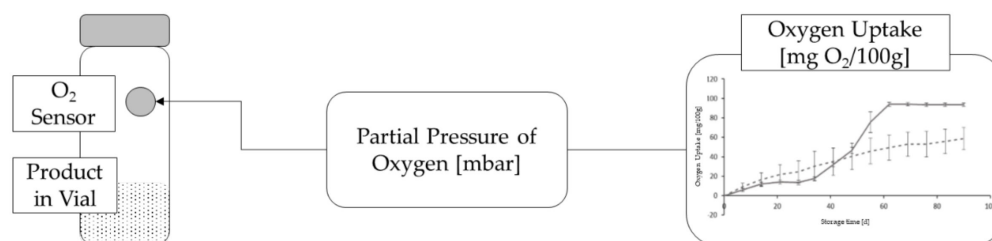
Figure 1. Scheme for experimental setup for measuring the oxygen uptake of emulsions during an accelerated storage test.

3. Results and Discussion

The rheological quality at the beginning of the measurement was stable and showed a glossy surface and smooth flow behavior of medium viscosity. It can be assumed that

the matrix behaved in the same way for all variants since no visual change in stability was observed in terms of change in viscosity, surface area, or phase separation after storage. The aerobic mesophilic total viable count was <5.0 cfu/g emulsion at the beginning of the storage, which was below the detection limit. Microbial metabolites such as CO_2 were below the detection limit of 0.1% in the headspace gas analysis in all vials after storage, which indicates that the possibly existing microorganisms have not multiplied. Therefore, it can be concluded that the samples were sufficiently preserved and oxygen was not consumed by respiring microorganisms. At the end of storage, it was observed that the oxygen sensors of almost all samples were intact and provided realistic results. One sample from the triple determination of phenethyl alcohol had to be excluded as an outlier due to leakage. The samples considered for evaluation showed average oxygen contents, which neither remained too close to atmospheric conditions nor approached zero absorbing the oxygen completely.

Using the headspace oxygen concentration results and the product weight, the oxygen uptake in mg oxygen per 100 g product (mg O_2/100 g) was calculated (Figure 2). The graph shows that the uptake of oxygen was greatest for the samples containing potassium sorbate and benzyl alcohol. The slope was very high at the beginning of the storage and flattened out during the later measurement points. Samples with ethanol and glyceryl caprylate remained constant and showed oxygen uptake around zero. Phenethyl alcohol was in the middle range but showed a slight decrease after initially strong oxygen uptake.
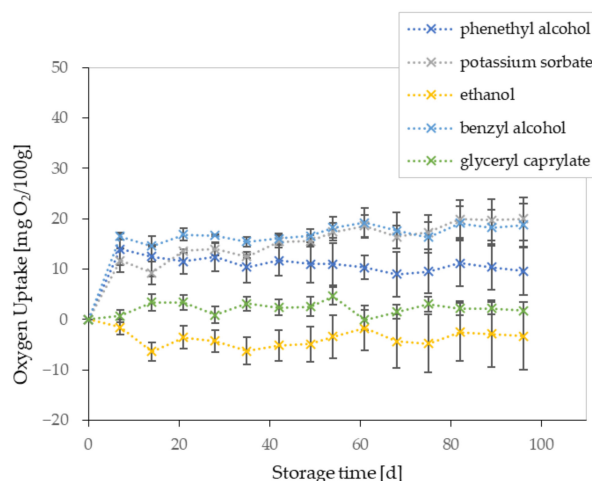

Figure 2. Development of oxygen uptake (mean $\pm$ standard deviation) (mg O_2/100 g) with different preservatives, calculated from the oxygen concentration in the headspace measured over a storage time of 96 days at 30 °C under light exposure.

It can be assumed that oxygen from the headspace was absorbed by the sample to form oxidation products due to the following reasons: Other oxygen-consuming reactions were unlikely since only unsaturated fatty acids in the lipid phase were able to absorb oxygen and microbial influences were excluded. Thus, the uptake of oxygen correlated directly with oxidation and the used preservative ingredient. As a result, oxidation can be assumed clearly for phenethyl alcohol, potassium sorbate, and benzyl alcohol. On the other hand, a decrease in oxygen uptake can be caused by a release of oxygen into the headspace by solved oxygen and air bubbles from the samples or from leaks in the seals of the vials. Due to the high gas barrier of the vial (glass), diffusion of oxygen through the vial material was basically not existent. It is unlikely that reactions had occurred that produce molecular oxygen. In all these cases, no oxidation would be measured. However, this affected only the samples with ethanol, where the oxygen uptake was below zero throughout the storage period. Although a slight increase in oxygen was measurable in the vials, oxidation was assumed to be not strong enough to compensate for this increase. The low oxygen uptake can be caused by the polarity change due to the high concentration of added ethanol since

the ethanol content in the water phase has an influence on the solubility of oxygen [65,66]. As the transfer of oxygen through the water phase to the micelles is the limiting factor for oxidation, an altered oxygen solubility could have an impact on oxidation.

For significance testing, a one-factor ANOVA with a significance level of 0.05 was applied to the oxygen uptake data after 96 days of storage. Mean values differed significantly (p-value = 0.0027). Afterward, a two-sample t-test (one-sided, with different variances) was used to test the significant differences between the two groups. The results are presented in Table 3. The oxidation of potassium sorbate was significantly higher than that of ethanol and glyceryl caprylate. The oxygen uptake of the variant with benzyl alcohol was significantly higher than with ethanol. Preservation with ethanol and glyceryl caprylate resulted in significantly lower oxidation than with potassium sorbate and benzyl alcohol. The other variants showed no significant differences.

Table 3. Significance of oxygen uptake (mg O_2/100 g) depending on used preservative after 96 days at 30 °C under light exposure between two samples using one-tailed two-sample t-test for different variances ($\alpha < 0.05$ = *, not significant = n.s.).

	Potassium Sorbate	Ethanol	Benzyl Alcohol	Glyceryl Caprylate
Phenethyl alcohol	n.s.	n.s.	n.s.	n.s.
Potassium sorbate		*	n.s.	*
Ethanol			*	n.s.
Benzyl alcohol				*

Furthermore, the daily oxygen consumption rate was calculated in mg oxygen per 100 g product per day of storage (mg O_2/100 g/d) based on the oxygen uptake data, which allows the estimation of the average oxidation rate (Figure 3). The diagram shows that the variants with potassium sorbate and benzyl alcohol absorbed the highest mean amount of daily oxygen consumption per day, while phenethyl alcohol, ethanol, and glyceryl stearate were the lowest. For ethanol, the value was also in the negative range, as in Figure 2, indicating that the oxidative processes were too weak to consume the oxygen entering the headspace. Since these data were calculated based on the data in Figure 2, the same argumentation can also be applied here, and the data can be interpreted as a measure of oxidation. The advantage of this representation is the estimation of the kinetics (oxidation rate per day) and the simplified summarized representation of a large volume of data.
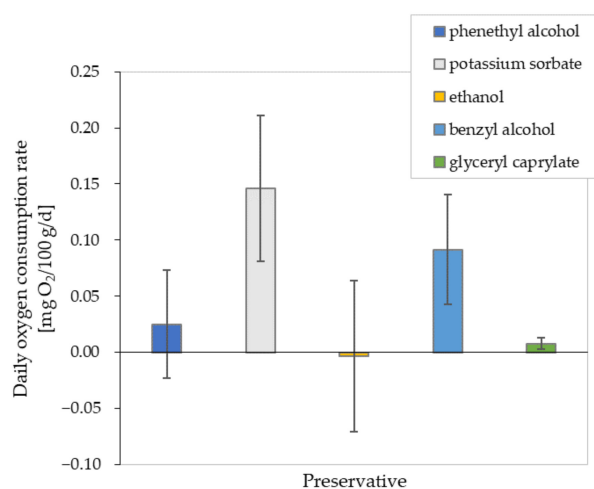

Figure 3. Daily oxygen consumption rate (mean ± standard deviation) (mg O_2/100 g/d) with different preservatives, calculated from the oxygen uptake measured over a storage time of 96 days at 30 °C under light exposure.

To test statistical significance, again a one-way factorial ANOVA and a one-sided two-sample *t*-test for different variances were used. The ANOVA provided no evidence of significant mean differences. The *t*-test showed that the daily oxygen consumption rate from the sample with potassium sorbate was significantly higher than with ethanol and glyceryl caprylate (Table 4). The other variants showed no significant differences.

Table 4. Significance of daily oxygen consumption rate (mg O_2/100 g/d) depending on used preservative after 96 days at 30 °C under light exposure between two samples using one-tailed two-sample *t*-test for different variances ($\alpha < 0.05$ = *, not significant = n.s.).

	Potassium Sorbate	Ethanol	Benzyl Alcohol	Glyceryl Caprylate
Phenethyl alcohol	n.s.	n.s.	n.s.	n.s.
Potassium sorbate		*	n.s.	*
Ethanol			n.s.	n.s.
Benzyl alcohol				n.s.

The comparison of both methods showed that the oxygen uptake delivered better the progression of oxidation with many data points, while the daily oxygen consumption rate better summarized the oxidation kinetics. Although the mean values of the daily oxygen consumption rate were comparable to the measurements of the oxygen uptake after 96 days, the standard deviation was clearly higher and made it difficult to prove significance. The reason for this could be that the calculation of the daily oxygen consumption rate also includes the values from the beginning of the measurement, where all samples did not show any differences in oxidation. The advantage of the daily oxygen consumption rate is that all data points are included in the calculation, and possible inaccuracies are less considered. The statistical evaluation of the oxygen uptake occurred only at the end of the storage, when the samples already had enough time to show significant oxidation. This improved standard deviation and significance testing but only considered a smaller number of data.

It can be shown from the data that potassium sorbate and benzyl alcohol had a pro-oxidant effect and accelerated the oxidation of the O/W emulsion strongly in this test, while phenethyl alcohol showed a moderate acceleration. Ethanol and glyceryl caprylate showed no oxidation accelerating effect in this test. These data are therefore consistent with the sources discussed earlier in the introduction. In order to describe whether ingredients significantly influence oxidation, as in this case, an experimental setup of at least 96 days at 30 °C with light exposure was suitable. Both parameters, oxygen uptake, and daily oxygen consumption rate can be used to determine oxidation. However, due to the lack of a blank sample, it was not possible to quantify how much the preservatives enhanced oxidation compared to a sample where preservatives were absent.

The oxidation showed a meaningful level for use in practice. Using the example of the sample with potassium sorbate, a total of 20.01 mg O_2 (0.32 mol) was absorbed per 100 g over the storage time. This is a high value compared with soybean oil, which contains also a high amount of linoleic acid and is no longer perceived as acceptable from 3–4 mg of absorbed oxygen per 100 g [67]. This low threshold may be caused by the high concentration of unsaturated fatty acids in plant-based oils, which oxidize and produce off-flavors faster. The emulsion in this study contained 22.80 g of canola oil per 100 g, of which 6.84 g was linoleic acid. This fatty acid can be converted to hexanal as the main oxidation product and has a perception threshold of 320 µg/kg oil (orthonasal) [68]. Data show after absorption of 57.05 mg O_2 per gram of linoleic acid (0.5 mol O_2/mol oil), a total of 7.65 mg of volatile products were found, of which 5.10 mg was hexanal [68]. Transferred to the data of this study, 100 g of the emulsion would only need to react with 0.36 mg of O_2 to reach the hexanal perception limit. Other studies described a rancid odor threshold for hexanal concentrations above 5 to 10 ppm in low-fat foods [69]. To reach this limit,

100 g emulsion should have absorbed just 5.59 to 11.19 mg oxygen. Assuming that 1 mol O_2 could lead to oxidation of 1 mol of oxygen-sensitive substances, a change in the shelf life, efficacy, and acceptance of the product is possible at the high intake of 0.32 mol O_2 per 100 g. While to the best of the authors' knowledge, there is currently no study in the literature describing the distribution of oxygen leading to oxidation and its shelf-life-limiting effects in O/W emulsions, it is likely that this low threshold could be reached and result in compromised quality.

To maintain the quality of cosmetic products, it is important to tolerate as minimal oxidation as possible. Therefore, pro-oxidant substances should be avoided, reduced, or compensated, even if preservatives are the cause of accelerated oxidation. It is recommended to investigate other preservatives and multifunctionals for their influence on oxidation in the future to discover possible alternatives or identify more unknown pro-oxidant effects. It is likely that preservatives or multifunctionals with similar molecular structures such as benzoic acid, anisic acid, phenoxyethanol, phenylpropanol, salicylic acid, or thymol may also have an effect on oxidation. Additionally, the question is whether molecules without unsaturated carbon bonds, such as levulinic acid, methylpropanediol, ethylhexylglycerin, or pentylene glycol, can influence oxidation. Optimization of the use concentration should also be considered, either by reduction, synergistic combination, or individual adaptation to the microbial risk of each application. Antioxidants can be used to compensate for the effect, for example, natural polyphenols, but their concentration should be optimized in further research, and possible synergistic and antagonistic effects with the preservatives should be investigated. In addition, synergistic or antagonistic effects with other cosmetic ingredients should also be studied to avoid negative effects such as the formation of benzene that was described for benzyl alcohol and ascorbic acid (vitamin C) [70]. Some ingredients such as tocopherols (vitamin E) can themselves lead to undesirable pro-oxidant effects if used in inappropriate concentrations [18,71]. Additionally, polyphenolic antioxidants are found to be pro-oxidants in high dosages [72]. Therefore, it is necessary to adjust the dosage of antioxidants individually to the ingredients contained. For future research, in addition to oxygen uptake, a quantification of volatile components is recommended and an organoleptic evaluation should occur to quantify the actual off-flavors in the emulsion matrix to correlate human perception with oxidation. It is of high interest to determine at which oxygen uptake value a significant change in the quality and efficacy or consumer perception of the product occurs and by what methods this period can be extended. Further data are necessary to verify how the preservative-caused oxidation can influence the shelf life of the products. Analysis of droplet size, rheological analysis, and analysis of oxidation products would also ideally enhance further research. Furthermore, it should be investigated whether the oxidation can also be transferred to W/O-emulsions or O/W emulsions with other ingredients.

4. Conclusions

The switch to natural and consumer-accepted preservatives requires rapid research and development of new active ingredients, but long-term shelf-life-limiting effects such as oxidation must also be taken into account. This could lead to reduced preservation of the oxidation-sensitive active ingredients and, thus, have a negative impact on the quality and efficacy of the product. In this study, potassium sorbate and benzyl alcohol showed significant pro-oxidant effects in the O/W emulsion tested. Both oxygen uptake and daily oxygen consumption rate were suitable for oxidation estimation. However, oxidation processes are highly dependent on the matrix and should be optimized individually for each product. These results indicate that other substances currently used as preservatives and multifunctionals could also have a negative effect on shelf life. Further research should be conducted to characterize these effects in more detail and to find methods to avoid or reduce them.

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