Oxidative decomposition of thin films of oleyl and stearyl alcohols on steel surface

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Fatty alcohols and their derivatives are popular additives in shampoos, cosmetics, paints, lubricants and other functional fluids, whose films are exposed to the environment. Often these films degrade due to oxidative, thermal, catalytic and other stress factors, producing volatile emissions. Decomposition of fatty materials is rarely viewed as a significant contributor to vapour losses, however, it cannot be assumed that fatty alcohols are completely non-volatile. In this study, oxidative degradation of thin films of oleyl and stearyl alcohols was investigated on the steel surface. Tests at 90 °C showed that within several hours significant portions of these alcohols were lost to volatile emissions. Initially the absolute evaporation rates did not depend on the film thickness and appeared quite similar for both alcohols. In later stages, the evaporation rate of thinner films went down due to the formation of oxidative polymers and functional group oxidation. Acidity of oleyl alcohol increased much more rapidly than that of stearyl. After long-term degradation oleyl alcohol produced gel-like solids, while films of stearyl alcohol began to retain a liquid state at room temperature. Since the volatile emissions amounted to more than 60%, the decomposition products in final applications should be investigated in more detail when stearyl or oleyl alcohols are used as major constituents in commercial liquids.

Keywords: oxidation, hydrolysis, catalysis, soaps

INTRODUCTION

The use of functional liquids in everyday life is rapidly expanding in the form of various cleaners, surface treatments, cosmetics, detergents, coatings, paints, lubricants, plasticizers, curatives and many others. Since the variety of employed chemical compounds is huge, major attention must be devoted to the safety of surrounding materials. Early disregard of health issues has turned into a very costly exercise when trying to remove a hazardous item from widespread articles. Many cases can be presented when compounds initially seem user-friendly based on superficial evaluation only, but after they are applied on a large scale, health problems appear as-sociated with their presence. Removal of such compounds from broad-spectrum materials has already resulted in major problems for consumers and manufacturers. Phthalate ester plasticizers have been linked to cancer, endocrine disruption [1], prenatal damages and other hazards. Diethanol amine had to be removed from shampoos and cosmetics due to nitrosamine carcinogen formation [2, 3]. The list can go on to include tricresyl phosphate in lubricants, formaldehyde and bisphenols in plastics and many others. Therefore, emissions from artificial compounds must be carefully analysed even in those cases when the material of interest has already achieved a large scale utilization.

Fatty alcohols are not widespread in nature, with only minor natural sources of their occurrence. Nevertheless, they are perceived as safe materials to use in many applications,

including indirect food additives. It is usually assumed that fatty alcohols do not produce hazardous decomposition products and their volatility is considered low, oleyl and stearyl alcohols in particular. These two and their derivatives show excellent surfactant, emollient, lubricant properties and many other desirable parameters. So they are widely used in shampoos, cosmetics, paints, lubricants, food industry materials, plastics and many other areas [4]. However, their vaporization and decomposition has not yet been studied extensively [5, 6].

In this study volatility and decomposition trends of oleyl and stearyl alcohol films are investigated with the purpose to assess the magnitude of their long-term emissions. Thin film settings were preferred to bulk liquids, because degradation proceeds much faster in films due to a dramatically higher exposure to air, humidity and metal surface. When the film thickness goes down below 10 microns, even electrochemical processes can take place [7] despite insulating properties of fluids with a low electrical conductivity. In addition, quite frequently these materials are exposed to environment not as bulk liquids, but as films in the form of coatings, layers, sheets and similar settings. Therefore, the film concept presents reasonable simulation of the actual degradation, which might take place in final applications.

In this investigation the degradation is simulated experimentally by a thin film degradation method, based on micro-oxidation [8, 9] family of tests. This concept is not the only one, which utilizes thin films for degradation testing, with more approaches available, such as Pressurised Differential Scanning Calorimetry (PDSC) [10], Panel Coker [11], TEOST-MHT [12] and others. However, the latter ones do not control the film uniformity, while PDSC and microoxidation allow large variation of the sample film thickness (Fig. 1).
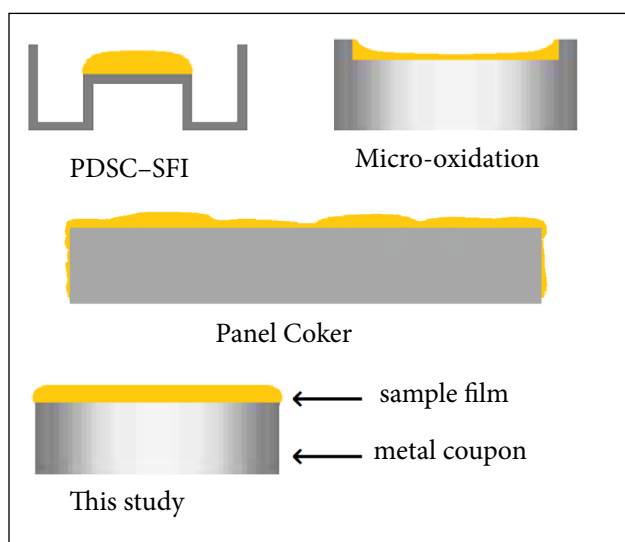

Fig. 1. Comparison of the sample film layout on coupon cross-sections in microoxidation [8, 9], PDSC–SFI [10], Panel Coker [11] tests and the current experiment

In microoxidation coupons, most liquid collects around the rim, with the center portion becoming very thin. Sample accumulation around the rim is evident in many PDSC sample pans as well, with the exception of Solid Fat Index (SFI) holder. This pan keeps the sample in a concave droplet layout, with a respective variation in its thickness. Obviously, PDSC needs specialized equipment and quite complex installations. In this study, a simplified version of a thin film was used as previously presented [13, 14], showing that the sample film retains a uniform thickness throughout the most part of the surface (Fig. 1). The temperature of 90 °C was chosen, since below 100 °C it is easier to retain some moisture, which might represent a major factor in degradation. Visual and gravimetric inspections as well as titrations were used to evaluate the degradation trends.

EXPERIMENTAL

Stearyl alcohol, CAS 112-92-5, was received as a free research sample of CO-1897 from Procter and Gamble (USA) with the reported m. p. 57 °C, C16–C18–C20 contents of 0.3%–99.1%–0.4%, respectively, Iodine Value below 0.0 and water contents of 0.01%. Oleyl alcohol of synthetic grade, CAS 143-28-2, was purchased from Merck GmbH (Germany) as Batch S6591123 with reported GC purity of 85.4% and density (20 °C/4 °C) of 0.848. Arachidic acid, CAS 506-30-9, was acquired from PMC Group (USA) with the reported melting point of 157 °F (~70 °C).

Most equipment and procedures, which had already been reported previously [13, 14], were used in this study as well. Low carbon steel coupons, whose top represented a relatively flat cylinder of 16–19 mm diameter (Fig. 1), were made internally and polished with the 2000 grit SiC abrasive cloth. Particular care was given to polish the sides of the cylinder in order to prevent the sample film from spilling over the brim of the coupon. The coupons were thoroughly washed with acetone, dried and weighed on the analytical balance ALJ-160-4NM (Kern An. Instr. GmbH) with ±0.1 mg accuracy.

The films of fatty alcohols were uniformly applied at pre-calculated amounts using a pipette and weighed to confirm that the needed thickness was achieved. Then the coupons were placed into a forced draft oven SNOL (Umega, Lithuania). In some cases, where separately indicated, a forced draft with a somewhat weaker air circulation HCP-108 (Memmert, GmbH) was also used. The temperature was maintained at 90 °C ± 1 °C for specified durations, then each coupon was removed from the oven and placed on a flat solid heat conductive surface of room temperature for cooling. After 10 min or longer the coupon was weighed to quantify vapour losses. Afterwards, the coupons were either washed off with isopropanol for acidity titration or placed back into the same oven for further degradation of 4 h or longer duration.

For acidity measurements, the degraded coupon was weighed, then washed with the solvent (acetone or

isopropanol), dried and weighed again, so the amount of the dissolved sample was determined. Only those degraded samples, whose solubility was nearly complete, were used for acidity determination. The washoff solution was further diluted with IPA and titrated per adapted ASTM D664 procedure using 0.01 to 0.1 M concentration solutions of KOH or NaOH in isopropanol and phenolphthalein as an indicator. Acidity was calculated as mg of KOH per 1 gram of the residual film.

RESULTS AND DISCUSSION

In this study, five distinct topics were investigated: 1) temperature equilibration issues; 2) significance of air circulation; 3) effects of film thickness; 4) comparison of vaporization intensity; 5) trends of acidity buildup. So the results are presented in this order. It must be noted that some details from the latter three topics have already been discussed in the previous report [6]. Also, some vaporization and acidity data, which has already been published elsewhere [14] as indicated in this report, is used to supplement the results of this investigation.

Temperature equilibration in sample films

The duration of sample film exposure to 90 °C ± 1 °C could not be strictly defined, because some period of time was necessary for the coupon to heat up when placed into the oven. After taking the coupon out, several minutes were also needed for the film to cool down. Temperature gradients are much higher during the initial stages of heating or cooling. Consequently, it takes a significant amount of time for the sample film to achieve 90 °C when heating up the film, but when cooling the coupon down, the sample film temperature drops very rapidly. This was clearly observed with the 500 µm film of stearyl alcohol. After placing the coated coupon into the oven for 5 min, the sample retained the flaky nature. Within 6–7 min the sample began to melt and became completely liquid after 7.5 min, as shown in Fig. 2.

It must be noted that the melting point of stearyl alcohol was reported at 57 °C, representing approximately a middle point between room temperature and test temperature. However, after taking the coupon out of the oven, the film solidified in less than 5 min (see the Table). This confirms that cooling proceeds fast and the film temperature drops significantly below 90 °C quite rapidly. Several more thicknesses of stearyl alcohol and arachidic acid were tested for better understanding of the melting process (see the Table).

T a b l e . **Observed durations, min (') and sec ("), of sample film melting when the coated coupon was placed into the oven at 90 °C ("Start to melt" and "Fully liquid") as well as heated film solidification when moved to room temperature**

	Theor. m. p.	Start to melt	Fully liquid	Start to solidify	Fully solid
Arachidic acid 500 µm	70 °C	9'	9'30"	1'50"	n. d.
Stearyl alcohol 500 µm	57 °C	7'	7'30"	3'10"	4'50"
Stearyl alcohol 200 µm	57 °C	6'	6'30"	3'20"	4'20"
Stearyl alcohol 100 µm	57 °C	5'	5'30"	3'	4'

The additional testing showed that film thickness also has some influence on melting or solidification trends. Being much heavier than the sample films, the coupon may act as a heat sink, nevertheless, the effect of film thickness is also important. As expected, thicker films require longer durations to reach the thermal equilibrium. A more extreme scenario was also investigated by melting arachidic acid, whose m. p. of 70 °C is much closer to the equilibrium temperature. Observations show that it takes 10 min or longer for the sample film to achieve 90 °C ± 1 °C after placing the coupon into the oven. Since the rates of evaporation and decomposition slow down very significantly with reduction in temperature,
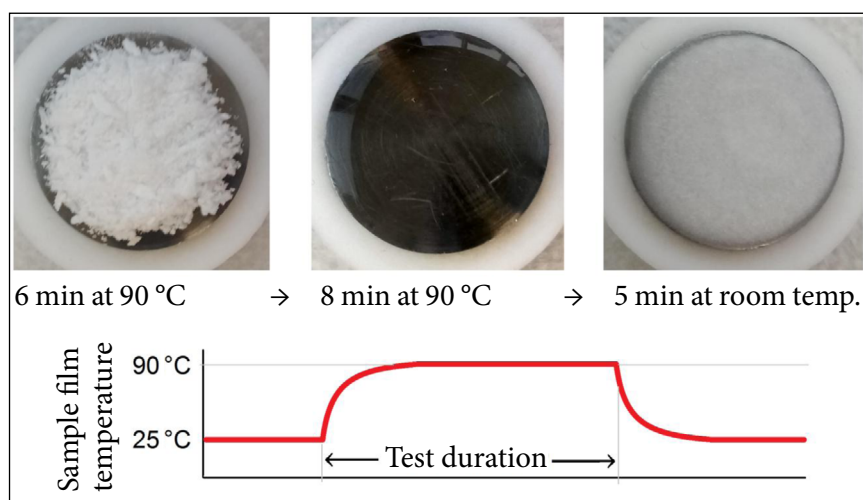

6 min at 90 °C   →   8 min at 90 °C   →   5 min at room temp.

Fig. 2. Top: photos of stearyl alcohol film (500 µm thickness) before, during and after placing into the 90 °C oven. Bottom: qualitative trends of sample heating and cooling during a thin film test

it can be assumed that any emissions or degradation stop right away with the coupon removal from the oven. But it takes more than 10 min (possibly much longer) to approach thermal equilibrium. Therefore, any data from the test durations shorter than several hours should be considered with adequate caution.

Influence of air circulation

Evaporation is strongly affected by convection on the liquid surface: waves, turbulence, airflow, drafts, etc. During the tests, extra caution is necessary to avoid shaking, vibrations, or other mechanical stress on the sample film. However, it would not be reasonable to perform the degradation tests in totally stagnant atmosphere, because evaporation would result in a buildup of partial vapour pressures of test compounds, slowing down the emission rate. Therefore, sufficient exchange between the oven compartment and laboratory air was needed in order to make the effects of partial vapour pressure negligible. It must be noted that fluctuations of air circulation intensity within the oven or between different ovens could present an undesirable variable. So gravimetrical measurements were made to compare the evaporation rates between two ovens (Fig. 3).

The testing results, which included some data from the previous reports [6, 14], showed that evaporation rates of both alcohols were quite similar, despite the data fluctuation. Influence of air circulation was not big, since both ovens had similar volumes and ventilation intensities. Still, the difference between the ovens was detectable after longer durations, such as 40 h. In the case of stearyl alcohol, weaker air circulation resulted in lower vapour losses, as expected. Data of oleyl alcohol was more scattered and did not demonstrate a statistically significant difference between the ovens. Nevertheless, the influence of air circulation is important and must be taken into account, especially when evaporation is rapid.

Effect of film thickness

If chemical processes are ruled out and thermodynamically ideal fluid is considered, its evaporation rate must depend only on temperature and convection. The latter factor is essentially dictated by the air circulation in the oven, as discussed in the previous chapter. Consequently, at 90 °C the evaporation rates should not depend on the sample film thickness, unless chemical reactions take place. Different film thicknesses were tested for both alcohols (Fig. 4).

In order to avoid additional data scatter, only the oven with stronger air circulation was used. The data shows that initially for both alcohols the evaporation rates of all film thicknesses remain within 0.1–0.2 mg/(cm^2 h). This is in agreement with the expectation that evaporation must follow thermodynamic laws, which also supports the validity of the thin film methodology. However, after the overnight testing the evaporation rates tend to be lower for thinner films, especially in the case of stearyl alcohol. This disparity increases with longer durations.

Such dependence of the emission rates on film thickness suggests that chemical processes take place in the films. On steel surface in air atmosphere, oxidation is nearly inevitable at 90 °C. As expected, stearyl alcohol should oxidize into octadecanal (i. e. stearyl aldehyde) initially (Fig. 5).

It should be noted that aldehydes are usually more volatile than respective alcohols due to lower affinity for hydrogen bonds. Unfortunately, no reliable data was uncovered to quantitatively compare thermodynamic parameters (boiling point, vaporization enthalpies, etc.) between stearyl alcohol and octadecanal. On the other hand, remaining oxidation products, as depicted in Fig. 5, appear clearly less volatile. Stearic acid and transitional polyhydric intermediates are more inclined to engage into hydrogen bonding than primary alcohols or aldehydes, therefore they are unlikely to evaporate from the film at 90 °C. Furthermore, stearic acid can undergo saponification on metal surface,
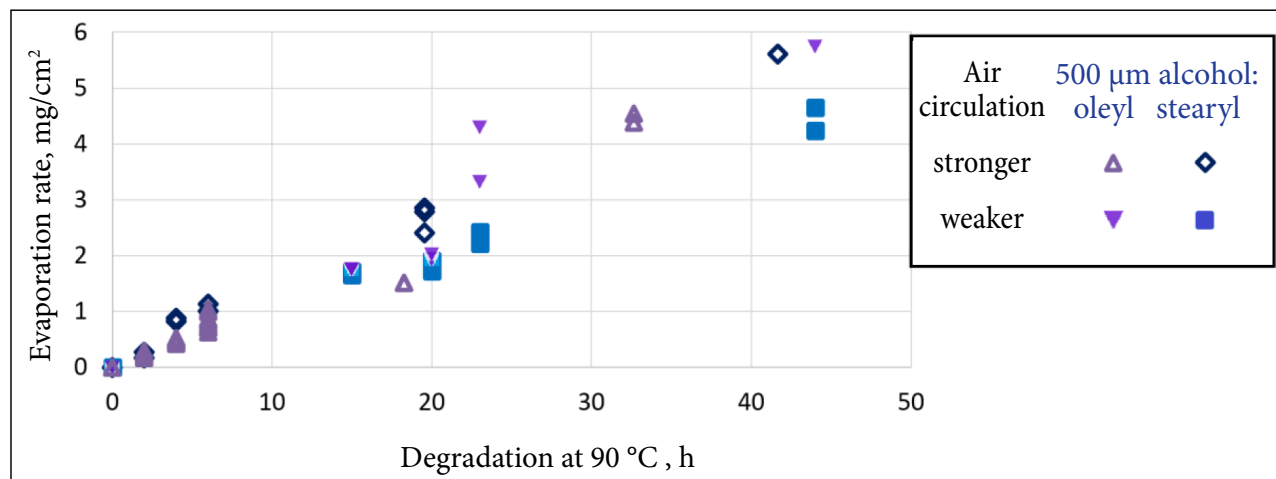

Fig. 3. Comparison between vapour losses of oleyl (triangles) and stearyl (squares) alcohol films of 500 μm thickness during degradation tests at 90 °C in a stronger air circulation oven (hollow symbols), and in a weaker air circulation oven (filled symbols)
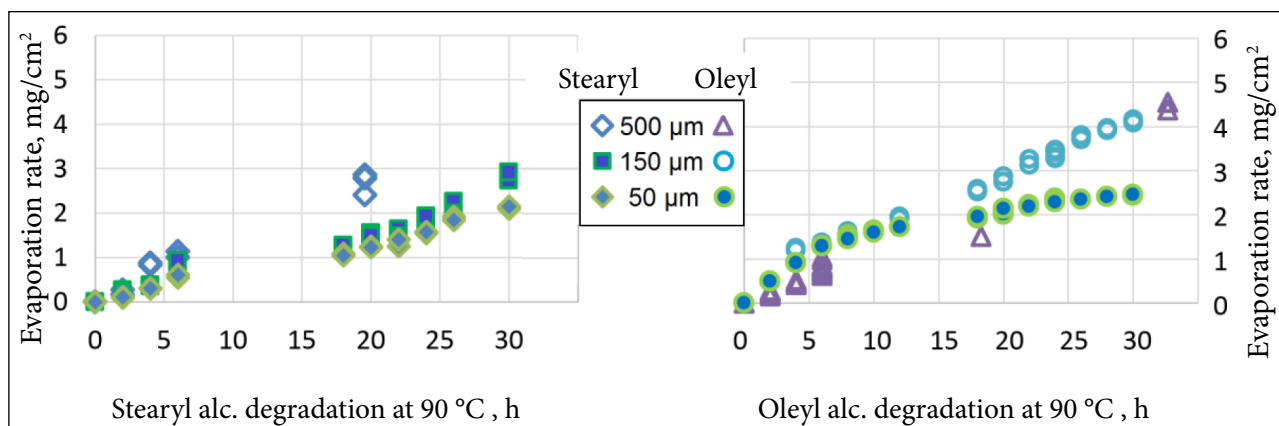
Fig. 4. Effects of sample film thickness on evaporation rates of stearyl and oleyl alcohols

forming Fe soaps, which are not expected to evaporate either.

Formation of such intermediates can also be supported by observing the degraded films visually. Due to m. p. 57 °C, the film of stearyl alcohol solidifies when taken out of the oven after less than 40–50 h degradation (see Fig. 2). However, after more than 100 h the film no longer solidifies at room temperature due to accumulation of various degradation byproducts. Such buildup of materials with lower volatility can reasonably explain why evaporation rates begin to recede sooner in thinner films of stearyl alcohol. Since total amounts of samples in the films of 500, 150 and 50 μm thickness are 45, 13.5 and 4.5 mg/cm², respectively, it is obvious that the whole sample could not evaporate. This was also clearly observed visually and quantified gravimetrically (Fig. 6).

While the vaporization trend of stearyl alcohol films did not deviate very far from linear, oleyl alcohol films showed much stronger disproportionality. Initially the thinner films of oleyl alcohol evaporated rapidly, while the 500 μm film did not change weight much. After 6–8 h the emission rate of the 50 μm film clearly went down, with the 150 μm film also showing some rate reduction. The emission rate of the 500 μm film did not decrease throughout the test dura-

tions in Fig. 6. These trends suggest that some other chemical processes take place in addition to formation of acids and soaps.

It is well known that unsaturated fatty materials undergo allylic substitution reactions during free radical attacks. With excess oxygen peroxides are readily formed, which eventually transform into hydroperoxides [15, 16]. The molecular weight of oleyl alcohol is 268.48 g/mol, while mol. wt. of its hydroperoxide is 300.48 g/mol already, i. e. 12% higher. Evidently, the 500 μm film of oleyl alcohol loses less weight than thinner films, because peroxide buildup compensates some of the volatile emissions. Peroxide formation proceeds throughout the whole film volume due to rapid oxygen diffusion, while evaporation takes place only from the film surface. Consequently, in thinner films the effect of evaporation is much more significant and the slowdown due to peroxide formation is less evident.

Vaporization during long term degradation
In addition to thermodynamic evaporation, during the film degradation a variety of concurrent processes take place: peroxide formation, buildup of acids, saponification and additional reactions. All mentioned ones and many others lead to mol. wt. increase, for example, oxidative polymerization,
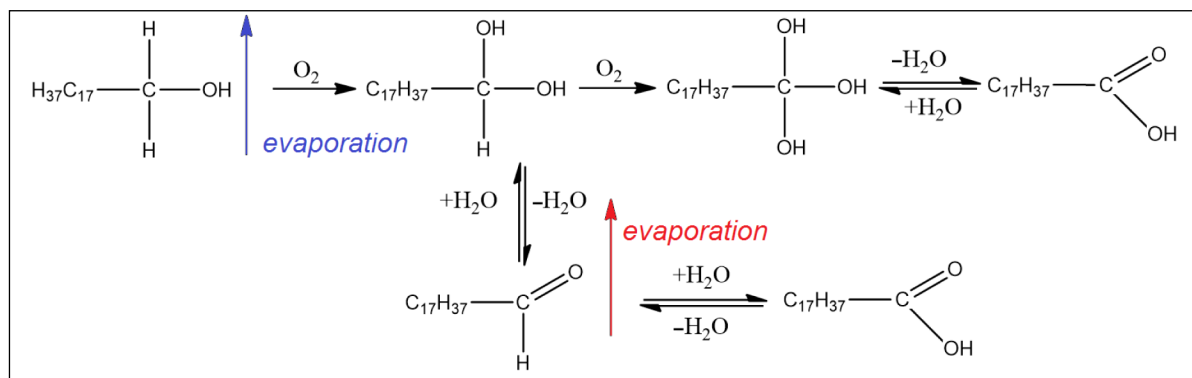

Fig. 5. Expected oxidation mechanism of stearyl alcohol with octadecanal and polyhydric derivatives as transitional products
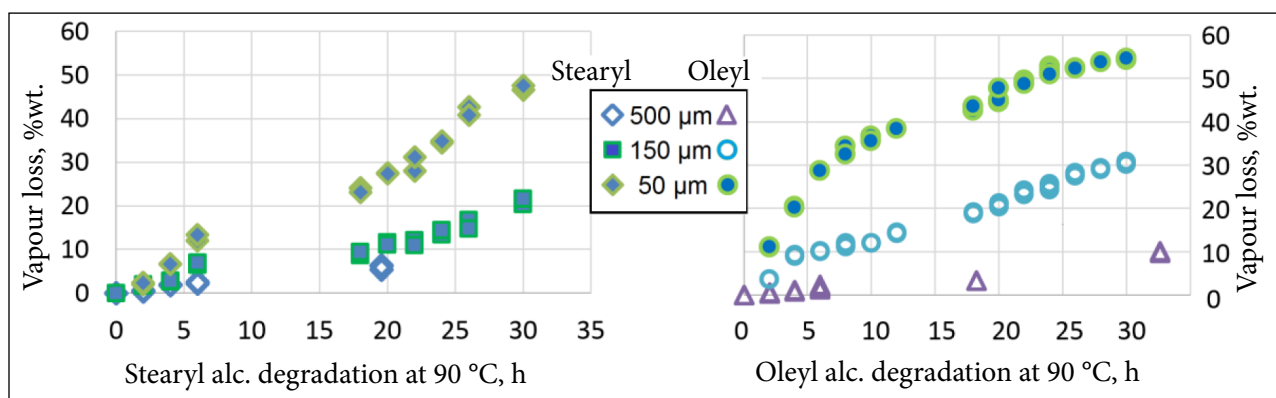
Fig. 6. Extent of vapour losses in terms of the total sample weight in the sample films of different thicknesses

epoxidation, Diels–Alder cycloaddition (due to linoleyl alcohol contamination), etc. However, some double bond reactions may generate lower mol. wt. products as well. The most prominent mechanisms relate to hydroperoxides, which are not stable at 90 °C. They easily decompose, frequently leading to fatty chain cleavage [17]. In the case of oleyl chain, the resulting double bond scission products usually contain just 4 to 10 °C atoms and should readily vaporise at 90 °C. Vapour losses due to these reactions are much more evident after longer test durations (Fig. 7, left).

The data in Fig. 7, which also included some measurements from the previous reports [6, 14], was acquired by using both ovens interchangeably, so the changes in the intensity of air circulation between weaker and stronger were not controlled. Consequently, the data scatter is somewhat larger, but qualitatively the difference is not overwhelming. It is evident that vapour losses of stearyl and oleyl alcohols are similar only initially. Before even approaching 100 h the emissions slow down very significantly in oleyl alcohol films. The linear-like evaporation rate lasts much longer in stearyl alcohol. If breakpoints were to be assigned to describe the emission slowdown, their estimates would fall around 90 and 180 h for oleyl and stearyl alcohol, respectively.

Another major difference between stearyl and oleyl alcohol films was observed, when the latter began to solidify after degradation for 240 h or longer [6, 16]. Its solidification was completely different than that of stearyl alcohol at room temperature, which was essentially driven by crystallization. While stearyl alcohol would melt when heated, the solidification of oleyl alcohol after 240 h degradation was irreversible, because the film remained gel-like when cooled and reheated. The film would not dissolve in organic solvents either. Around 200 h the early signs of solidification were observed in a form of solid texture near the brim of the coupon. Later a thin top layer would form, which would float on the surface of the sample when touched with a spatula. The top layer would grow rapidly and after 240 h the oleyl alcohol samples appeared fully solid. Therefore, the tests of oleyl alcohol were limited to less than 240 h except for several data points around 270 h, which

were collected after the film solidification. It must be noted that convection and diffusion in solid films are much more restricted, which dramatically reduces the evaporation rates.

Solidification of oleyl alcohol is a result of oxidative polymerization (a.k.a. oxypolymerization [18]) because of high mol. wt. Oxidation products are generated, which are no longer soluble in original fluid. Their abundance might be so high that gelation processes could take place. Visually, the solidified film appeared gel-like and demonstrated some swelling in organic solvents. However, additional experimental efforts would be necessary to study the details of solidification mechanisms.

Acid buildup during long-term degradation
It is well known that acids are formed in fatty materials during degradation due to several reasons:
- oxidation of the functional group from hydroxyl into carboxyl (as discussed above, Fig. 5);
- hydroperoxide decomposition;
- decomposition of polyunsaturated contaminants (e. g. linoleyl alcohol);
- other mechanisms: ozonolysis, microbial degradation, UV exposure, etc.

Kinetics of the functional group oxidation must be rather similar for both alcohols, because their mol. sizes are nearly the same and the functional group is quite far from the double bond, which represents the sole intramolecular difference between stearyl and oleyl alcohol. In contrast, hydroperoxide decomposition is very different between the two samples. Free radical attacks on stearyl alcohol are less frequent, because the only weaker site can be associated with the C–H bonds at β-carbon position [19]. The other C–H bonds are nearly identical, which makes the free radical attacks less probable. Oleyl alcohol has a C=C double bond, which is much more vulnerable to free radical attacks. Allylic substitution reactions take place much easier, so it is assumed that degradation of mono-unsaturated chains (like in oleyl alcohol) is approx. 10 times faster than that of saturated ones (i. e. stearyl).
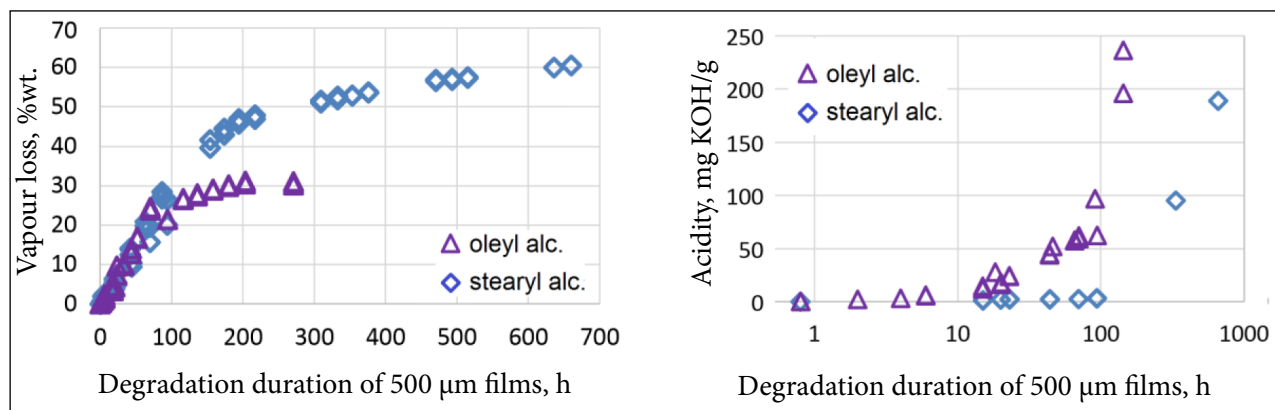
Fig. 7. Effects of long-term degradation of 500 μm films on (left) vaporization tendencies and (right) acidity buildup

Other possible mechanisms were not applicable for stearyl alcohol, because it did not contain unsaturation (as supported by Iodine Value of 0.0). The samples were not exposed to ozone, UV or biological factors either. Consequently, it can be assumed with some precaution that stearyl alcohol acidifies mostly due to oxidation of the functional group (Fig. 5). To the contrary, in oleyl alcohol not only functional group is oxidized, but also the double bond leads to hydroperoxide formation and eventual decomposition with acid buildup. In addition, contamination with linoleyl alcohol or other polyunsaturated constituents could not be ignored in oleyl alcohol because the sample purity was less than 86%. Polyunsaturated material is much more susceptible to free radical attacks due to the presence of bis-allylic hydrogens. Also, additional chemical reactions become available in polyunsaturated chains, such as conjugated double bond formation, Diels Alder cycloaddition [20] and similar. The exact amount of unsaturation was not determined in this study, but the sample itself was nearly colourless, suggesting that the polyunsaturation contents were low.

Titrations confirmed the expectation that oleyl alcohol formed acids much faster than stearyl (Fig. 7, right). Acid buildup in stearyl alcohol was not linear, being very slow initially and then accelerating until the test termination after 670 h. In oleyl alcohol the acid formation rate seemed to accelerate with time as well, until film solidification. The last titrations of oleyl alcohol films were performed after 160 h degradation, because the longer durations would lead to solubility problems, despite an apparently liquid film.

Long-term degradation shows that stearyl alcohol can approach the acidity of 200 mg KOH/g. Such value is typical for pure stearic acid. However, it is evident that some acids form soaps, which probably should not act as free acids during the titration. Most likely, significant degradation of the fatty chain takes place during long-term testing and results in additional acid functionalities. Obviously, the whole scenario is quite complex making it difficult to relate the gravimetrical data to exact chemical reactions. Never-

theless, high acidity of degraded stearyl alcohol suggests that oxidation takes place on C–C chain as well via hydroperoxide formation and eventual decomposition. Therefore, thermodynamic evaporation must not be viewed as the sole source of volatile emissions from stearyl alcohol films.

It is evident that thin films of both oleyl and stearyl alcohol easily form acids and generate large amounts of volatile emissions in long-term degradation. The amount of material lost from thin films at 90 °C can exceed 60% wt. depending on the film thickness (Fig. 6). The residual films may solidify in the case of oleyl alcohol, but still continue to degrade. Evidently, the volumes of volatile losses are appreciable in both oleyl and stearyl alcohol. Therefore, paints, lacquers, coatings, shampoos, lubricants and other commercial liquids should be investigated in more detail to better understand the character of their emissions.

CONCLUSIONS

1. A thin film test can effectively quantify long-term volatile emissions of liquids, because degradation in films is much faster than that in bulk liquids.

2. Evaporation rates do not depend on film thickness, however, with further degradation compounds of higher mol. wt. build up, slowing down the emissions.

3. Oleyl alcohol degradation leads to irreversible gel-like solidification of the whole film. Degradation of stearyl alcohol (m. p. 57 °C) eventually results in retention of the liquid phase at room temperature.

4. As expected, fatty alcohols oxidize into fatty acids due to availability of air and metal surface. Oleyl alcohol acidifies faster than stearyl alcohol due to oxidation of double bonds.

5. Since amounts of vapour losses can exceed 60% wt. from the whole sample, a more detailed study is needed to evaluate the chemical nature of volatile emissions from paints, lacquers, coatings, shampoos, lubricants and other commercial liquids, which may contain significant treat levels of oleyl or stearyl alcohols.

ACKNOWLEDGEMENTS

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PLONŲ OLEILO IR STEARILO ALKOHOLIŲ PLĖVELIŲ OKSIDACINIS IRIMAS ANT PLIENO PAVIRŠIAUS

S a n t r a u k a

Riebalų alkoholiai ir jų dariniai plačiai naudojami kaip priedai šampūnuose, kosmetikoje, dažuose, tepaluose ir kituose skysčiuose, kuriais padengti paviršiai yra veikiami aplinkos. Dažnai tokios plėvelės degraduoja dėl oksidacijos, šilumos, katalizinių ir kitų agresyvių veiksnių susidarant išlakoms. Į riebalinių medžiagų skilimą retai žiūrima kaip į reiškinį, susijusį su išgaravimu, tačiau negalima teigti, kad riebalų alkoholiai yra visiškai nelakūs. Tyrime analizuojamas oleilo ir stearilo alkoholių plėvelių oksidacinis irimas ant plieninio paviršiaus. Atlikti bandymai 90 °C temperatūroje parodė, kad per keletą valandų didelė dalis šių alkoholių išgaravo. Kaitinimo pradžioje alkoholių plėvelės storis neturėjo įtakos absoliučiai garavimo spartai, kuri buvo beveik vienoda abiems alkoholiams. Vėlesniais etapais plonesnių plėvelių garavimo sparta sumažėjo dėl oksidacinės polimerizacijos ir funkcinės grupės oksidacijos. Oleilo alkoholio rūgštingumas didėjo daug greičiau nei stearilo alkoholio. Po ilgalaikio kaitinimo oleilo alkoholis įgijo gelio pavidalą, o stearilo alkoholis pradėdavo skystėti jau kambario temperatūroje. Po ilgos trukmės degradacijos daugiau nei 60 % plėvelės virto lakiais irimo produktais. Tais atvejais, kai stearilo arba oleilo alkoholiai yra naudojami kaip pagrindinės sudedamosios dalys komerciniuose skysčiuose, derėtų detaliai ištirti galutinio produkto oksidacinio irimo procesus.