Oleochemicals – important additives for building protection

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Abstract: Oleochemical raw materials, namely metal soaps and sodium oleate are characterised by a beneficial cost/performance ratio. The water absorption coefficient (w) in water resistant plasters has to be below 0.5 $kg/m^2h^{0,5}$. To achieve this, metal soaps are widely used. A dosage of 0.3% of Zinc or Calcium Stearate is sufficient to attain this specification. An essential criteria in this application is the quality of the stearate. Mainly precipitate stearates, with their high specific surface, perform well. A hydrophobic render always has purer wetting properties when mixed with water, however, this could be a disadvantage at higher concentrations of the stearate. The use of sodium oleate could be beneficial in this instance. The product itself acts as a kind of surfactant / plasticizer in the render. During the setting of the render, a reaction with calcium ions in the cement or limestone takes place and the oleates are transformed to hydrophobic metal soaps. The interaction with other raw materials in the plaster formulation is much more pronounced. Mixed products of stearates and oleates could be an answer to this problem. There are different qualities with variable ratios of oleate to stearate content available, specifically blended for different applications, for example, scratched plasters, repair mortars, reinforced renders, etc.
Keywords: Plaster, Hydrophobic Agents, Oleochemicals, Stearates, Oleates

1. INTRODUCTION

A natural decline process occurs in almost all things we perceive in our environment. Wherever possible, human beings try to protect their values against this process. This protection can also be applied to buildings, because they are clearly visible signs of human creativity and they decline when they are subjected to the adverse affects of the environment.

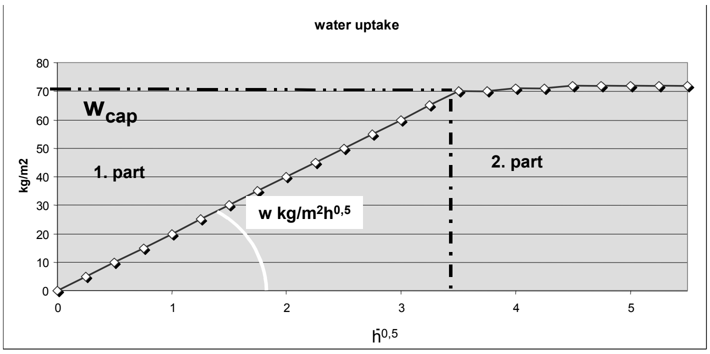
Water is the most common cause of serious damage. It is responsible for the transport of harmful substances like salts, promotion of the growth of micro-organisms and frost damage in cold periods. Also, heat transition is directly linked to the amount of moisture in building materials. But there are effective ways to protect them against water decay.

The construction chemistry performs moreover an important contribution while making effective and economic hydrophobic agents available. However, the successful application of these materials is directly linked to deeper knowledge of the function and also the interaction with other construction materials.

This paper will give a brief overview about the chemistry and properties of oleochemical use in construction. This will be followed by highlighting the various application areas of as hydrophobic agents based on oleochemicals.

2. WATER ABSORPTION OF BUILDING MATERIALS

The water uptake of building materials can only be carried out through their capillary system and is given by the "square-root-of-time law". If water absorption is plotted against the square root of the time, a straight line results (figure 1). The water uptake coefficient (w) is defined as the slope of the first stage of the cumulative inflow curve as a function of the square root of time.



W =	$w * \sqrt{t}$
W =	water absorption [kg/m2]
w =	water absorption coefficient [kg/m2h0,5]
t = time [h]	

Figure 1 – Square-root-time-law for water absorption of building materials

The first part of curve describes the capillary dominated part. The second one is influenced by contribution of air in water.

3. CHEMISTRY AND PROPERTIES OF OLEOCHEMICALS FOR THE BUILDING INDUSTRY

Generally, metal soap means a fatty-acid salt of any metal. In practice, however, there is a big difference in the chemical and physical behaviour. Salts of alkaline metals are soluble in water and act like surfactants. Alkaline earth metals and other bi- or trivalent metals form water insoluble, highly hydrophobic salts. Also, the fatty acid part of the salts can be different. We can distinguish between two main categories, saturated and unsaturated acids. The most important representative of the first group is stearic acid. Like the others, it is obtained from natural sources, therefore it is not a pure C18-fatty acid, but a mixture of various linear-chain fatty acid, mainly of the chain length C16 and C18. From the group of unsaturated acids, oleic acid is mainly used in the building industry, this is also not a chemically pure substance. As shown in figure 2, four main categories of oleo-chemicals are of importance in terms of use.

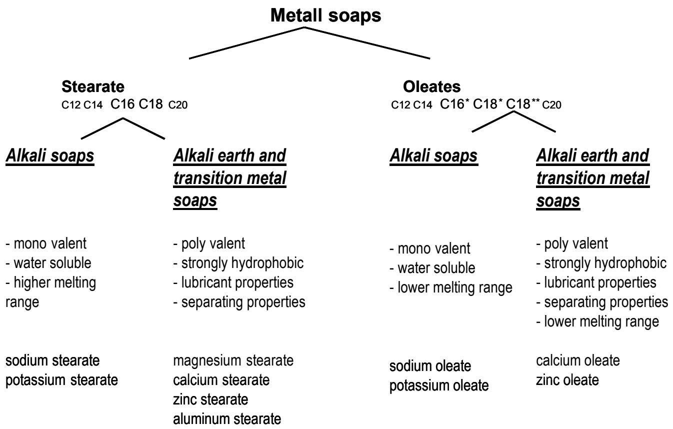


Figure 2 Categorization of soaps and metal soaps

3.1 Metal soaps

The quality of alkaline earth and transition metal salts is predominately linked to the production method. The most important commercial methods are precipitation and direct processes. The stearates obtained by precipitation are characterised by high specific surface and low bulk density. A high specific surface is essential for the performance because a higher surface area of the building material is covered with the hydrophobic substance. Stearates produced by the direct process have a higher bulk density and lower specific surface. For this reason, precipitated stearates are preferred for building protection. The reaction is described below:

1. $2\ NaOH + 2\ CH_3(CH_2)_{16}COOH \rightarrow 2\ CH_3(CH_2)_{16}COONa + 2\ H_2O$
2. $MeCl_2 + 2\ CH_3(CH_2)_{16}COONa \rightarrow (CH_3(CH_2)_{16}COO)_2Me + 2\ NaCl.$

3.1.1 Influence of the specific surface

For a certain hydrophobic effect, it is sufficient to cover the most active surfaces of the building material, e.g. edges and spikes[1]. Therefore the conclusion is evident, that a product with a high specific surface offers the best results.

Table 1 – Properties of two different zinc stearates used in standard render (0.25 %)

Product	Bulk density [g/l]	Sieve residue 45 µ [%]	Spec surface (calc). [m^2/g]	w [kg/m² $h^{0,5}$]
Zinc stearates I	160	5	12	0.35
Zinc stearate II	280	0.6	8	0.57

Since the determination of the specific surface is complex, it is much easier to compare the bulk density of various products; keeping in mind that it is directly linked to the specific surface. Metal soaps with low bulk density conversely have a higher specific surface (see Table 1).

It is also evident from Table 1 that a milling process is not suitable to achieve a higher hydrophobic effect, the product with a higher sieve residue offers better properties.

3.1.2 Influence of the fatty acid anion

As previously discussed, the stearates are not based on the pure stearic (C18)-fatty acid. They more or less show a distribution of C chains from C12 to C22 predominately C16/C18. From a theoretical viewpoint, acids with longer C-carbon chain exhibit a better hydrophobic effect. Functional groups or double bonds decrease this effect. Riethmayer[2] has experimentally investigated this relation and found the dependence shown in Figure 3. In practice however, no such adverse influence of the fatty acid on the water repellence could be found. Also laurates (C12), in some formulations, also gave good results. A reason for this could be that these salts could have a better distribution in building material.

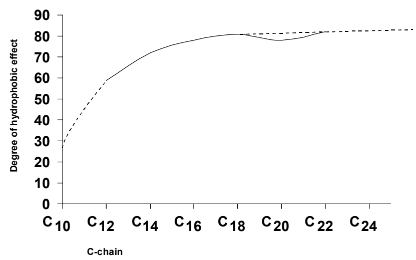


Figure 3: Influence of fatty acid on the water repellence

3.1.3 Influence of the cation

Similar to the anion, the fatty acid, the type of the cation used will have an influence on the properties of a metal soap. It is to be expected that cations with a higher electron affinity show slightly reduced hydrophobic properties. The water repelling effect of the metal soap is reduced with an increase in the atomic number. In practice, salts of calcium, magnesium and zinc are used with good success. Beside this theoretical background, there are also strong regional differences in Europe. In Austria, Germany and Switzerland, Calcium and Zinc are preferred while the French building industries by tradition use magnesium salts. As an additional advantage, Zinc stearate also confers a slight algaecide effect. Although this is not sufficient to protect plaster from the growth of micro-organisms, it could be considered as an additional benefit, especially in the context of the changing climate conditions.

3.1.4 Influence of the functional groups

For the trivalent Aluminium Stearate a reduction of hydrophobicity from the tri to mono stearates could be found. This is reasonable in the chemical structure of these compounds. Aluminium-di-stearate has another free OH-group while Aluminium-mono-stearate has two. In particular this property can also be an advantage, e.g. at polar surfaces, which are easier to cover with stearates. Generally, over based metal soaps, used as a stabilizer in PVC, are less suitable for the application in the building industries.

3.2 Water soluble soaps

The above explanations show that metal soaps are ideal water repellent agents for mineral plasters. The main downside in use is, however, the difficult wettability of the dry mortar. An answer to this problem was found in the formation of the water-soluble soaps. Soaps of unsaturated fatty acid are readily soluble in water. They act like surfactants and exhibit dispersing properties. Due to their high affinity to calcium ions, they are transferred in the plaster to the hydrophobic metal soaps. As this reaction is essential to get the hydrophobic effect, these types of product are also considered as 'Reactive Hydrophobic Agents'. Hydrated lime as well as cement can act as a calcium source. The formulators of building materials should, when using reactive agents, always keep in mind, that a sufficient supply of calcium ions is essential for this application. The efficiency of reactive product is quite higher than the use of stearates. This is justified by the better distribution in building materials as well as an improved coating behaviour (see Fig. 4). It is also important to mention that the formation of the hydrophobic metal soap is temporarily delayed. This offers the opportunity, to use soluble soaps preferably in base renders.

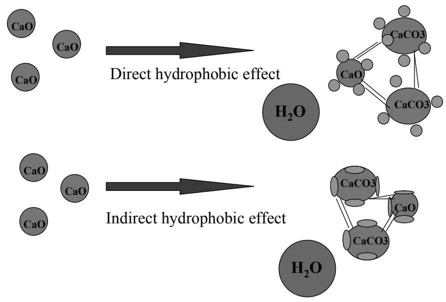


Figure 4: Direct and indirect hydrophobation

3.2.1 Sodium stearate

Sodium stearate shows the highest swelling capacity of the alkali soaps. Therefore, it is used in concrete as a sealing agent. This effect is caused by the formation of gels when it comes in contact with water. The gels block the capillary system of the building material and cause the hydrophobic effect. This property of the sodium stearates is subject to an aging process and declines with time[3]. Sodium stearates are also soluble in water, but rather slower in cold water. Therefore, the swelling effect dominates and the efficiency is lower than those of unsaturated sodium salts.

3.2.2 Sodium oleate

Sodium oleate has achieved the biggest importance as a reactive hydrophobic agent. Due to the high content of unsaturated fatty acids it shows no gelling effect. The solubility in cold water is significantly better. In building materials with sufficient calcium content, the reaction to metal soaps dominates.
Compared to metal stearates sodium oleate shows a higher bulk density and can be produced in a coarse structure, as the specific surface of the product itself is of minor importance. Free flow ability, reduced dust formation and improved solution behaviour are the main focus for improving the physical form of sodium oleate. The key to the quality of oleate is the C-chain distribution. Neat oleic acid should have a high content of mono unsaturated C18 acid. The amount of polyunsaturated acids should be controlled. They show less hydrophobicity and also the long-term stability is less. C-chain distribution should be of high consistency. The interaction with other building materials is much higher than those of the metal stearates, especially with air entraining agents and cellulose ether. The apparent density of the mortars are higher, the amount of air bubbles is reduced. This could be easily adjusted in the formulations, but variations in quality make this very complex. Therefore, the C-chain distribution should be of high consistency.

3.3. Combined products

The drawback of using sodium oleate is the delayed effect of the water repellency and the very different behaviour of sodium oleate and metal stearates in building materials. It was suggested to combine the metal soaps and sodium oleate to produce a product which gave the optimum properties required for the building industry. By varying the ratio of metal soap to oleate a wide range of products are now available.
The soap part in the products acts like a dispersing agent and lends towards an optimal distribution of metal soaps. These in turn decrease the influence of the mixture on air content and open time. As opposed to common dispersing agents, the oleates lose their surfactant properties with the formation of the corresponding metal salt in the building materials. Another advantage of mixed products is the much quicker formation of the water repellence properties. To summarise, the combined products are characterised by a very versatile end use.

4. Application

The different oleochemical products used in the building industry are referred to in Section 3. The following give recommendations for application in various building materials.

4.1 Dry mortars

For renders, the following general rules can apply:

- metallic soaps mainly used in finish coatings, concentration 0.3-0.8 %
- metallic soaps have minor interactions with other raw materials in the formulation
- metallic soaps exhibit no significant influence on the hydration behaviour of cement
- sodium oleate is advantageous in base renders, concentration 0.1-0.5 %
- sodium oleate shows delayed formation of the water repellent effect
- sodium oleate shows interaction with air-entraining agents and cellulose
- the content of the air space decreases
- sodium oleate acts as a plasticizer
- the time of the dry mixing is less critical
- sodium oleate has no “creaming” effect
- combined products are universally utilizable hydrophobic agents
- the influence of the content of air voids is in between sodium oleate and metallic soaps

These rules can only give some indication on proper usage. In practice, other factors have to be taken into consideration, namely logistic issues, dosage possibilities, as well as the company- and purchasing philosophy. With all three product groups, neat building materials could be made. Of more importance is a better understanding of the different behaviour of the hydrophobic agents in order to answer the challenges from different applications.

4.2. Dosage of Water Repellent Agents

From theoretical calculations, a dosage of significantly less than 1% should be efficient for the use of stearates. As shown in Figure 5, the strong decrease in the w value at low concentration is founded on an easy covering of the most reactive surfaces. Further hydrophobation needs much more effort. It is also demonstrated that sodium oleate has better

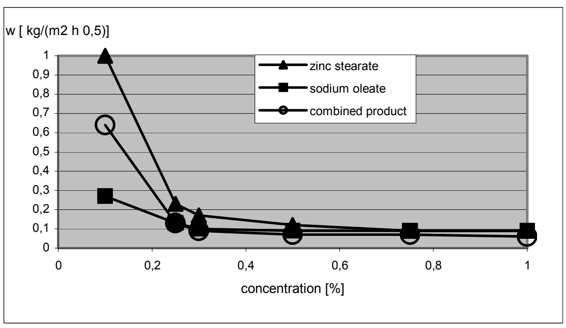


Figure 5: Dosage of some water repellent agents in standard render (see Table 2)

efficiency. As expected, the combined product falls in between. All tests were carried out with a standard formulation shown in Table 2.

Componet	[%]
Binder:	
Cement: CEM I 42,5 R	15.0
White hydrated lime: CL 80	3.0
Addition:	
Limestonemeal	12.0
Limestonesand 0 – 0,5	40.0
Limestonesand 0,5 – 1,25	30.0
other additives:	
Methylhydroxyethylcellulose	0.10
Starch ether	0.01
Air entraining agent	0.02
Hydrophobing agent:	

Table 2 – Standard render

4.3 Influence of Hydrophobic Agents on Plaster Properties

As shown in Figures 6 and 7 a hydrophobic agent has an influence on the consistency as well as on the air content of a plaster.
As an indicator for the consistency, the water consumption is plotted against the concentration of the stearate. The slump of the mixture was adjusted at 17 cm by using a flow table.

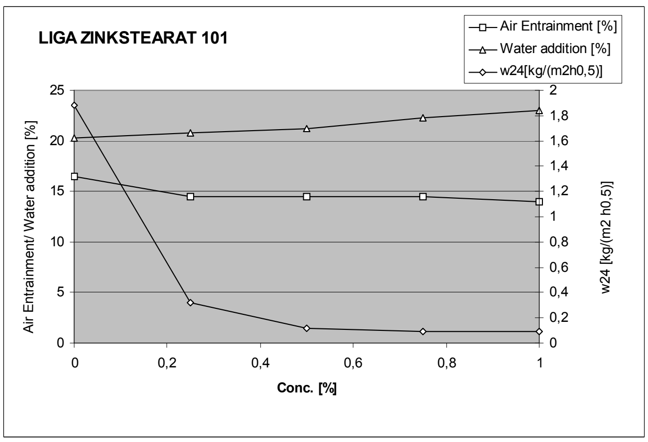
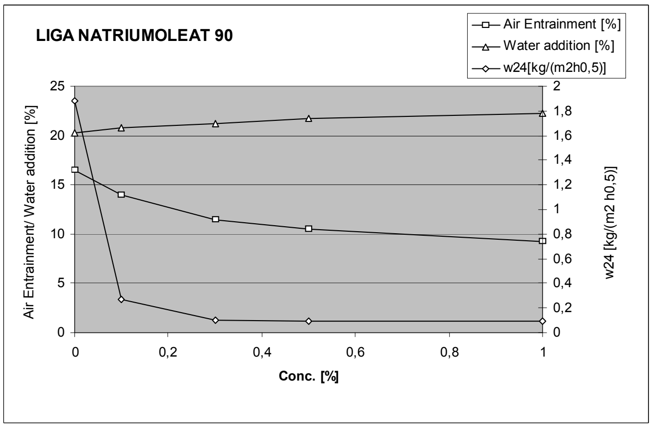


Figure 6: Dosage of zinc stearate in standard render (see Table 2)

Both a direct hydrophobic agent, like the zinc stearate, and the reactive sodium oleate, show in principle the same influence on water consumption.
With increasing additions, the water consumption also rises. For stearates, this behaviour is expected, but oleates with their surfactant properties should work like plasticizer and therefore reduce the water consumption. It was concluded, that interaction with other raw materials had an influence. Also the wetting of the surfaces in the plaster may be raised and therefore the water consumption is higher.

Using hydrophobic agents also decreases the air entrainment in plaster. Stearates show less influence on air entrainment due to their defoaming properties as very fine particles. There is no interaction with other ingredients in the recipe. Sodium oleates however have interaction with the surfactants used as air entraining agents. Normally the amount of foam from anionic surfactants is suppressed by alkaline soaps. Non-ionic surfactants are less sensitive. The type of cellulose ether is important in this relation.



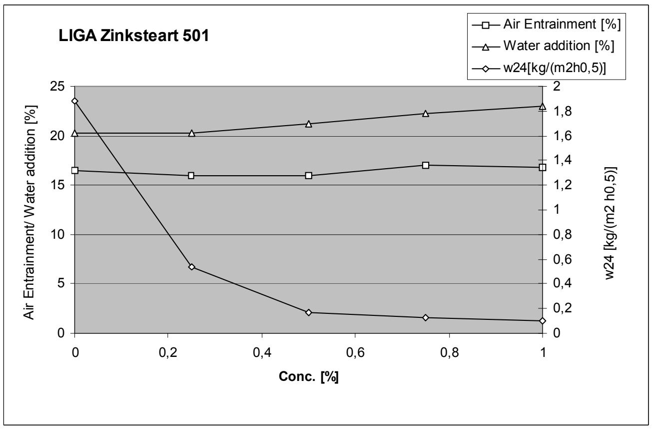


Figure 7: Sodium oleate and modified zinc stearate in standard render (see Table 2)

It is also shown in Figure 7 that this behaviour could be changed by using additives. The LIGA ZINKSTEARAT 501 type is a mixture of zinc stearate and a free flowing agent. The influence on the air entrainment is very low and more or less stable.

4.4. Concrete

In the production of concrete mainly liquid products are used. Therefore stearates in their watery dispersion form are preferred, for example, Calcium stearate 50 % in water. They show a dual mode of function. On one hand they act as a fluidizer and break the capillary system. On the other hand, the stearate covers the inner surfaces and makes them hydrophobic. The area of application is e.g. paving stones. The primary aim is to reduce the blooming of salts which cause a visual degradation of the surfaces. The frost, salt and soil resistance is also improved. In Figure 8 the degree of hydrophobic setting is given in relationship to the concentration of hydrophobic agent calculated on the amount of cement. To measure this effect, paving stones are made with different concentrations of stearate dispersion. For a period of eight months they are weathered and sprayed with water. The degree of hydrophobation was optically measured on the surface as a percentage of blooming capacity of the salts. Good results are given even at a concentration of 0.8% of calcium stearate in dispersed form. The sigmoid form of the curve is given by the dual function. It shows the typical saturation behaviour.

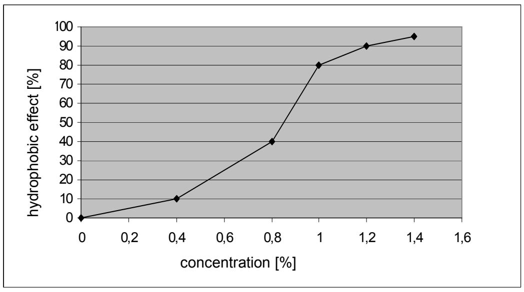


Figure 8: Influence of calcium stearate on the hydrophobic effect of concrete

4.5 Joint Fillers

The hydrophobisation of joint fillers show the following benefits:

- Improved frost resistance in outdoor environment,
- Improved resistance against corrosion caused by water soluble salts,
- Improved soil resistance
- Protection against the growth of micro-organisms.

All three types of hydrophobic agents are used. The requirements on the quality of joint fillers are very complex. The most important ones are open time, shrinkage, water retention and adhesive properties. As stearates show minor interactions with other raw materials, they are the first choice. It could be very beneficial to mix them with re-dispersible powders. The distribution of the stearate is improved and also some mechanical properties such as the adhesive behaviour.

4.6. Influence of the mixing intensity on the water repellency

Theoretical considerations on water repellent treatment with oleochemicals suggest, that intensive mixing of dry mortar would result in better hydrophobicity[4]. The degree of covered surface should be higher. Riethmayer[4] verified this assumption as shown in Figure 9.

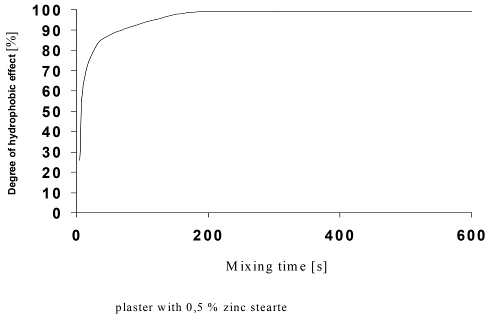


Figure 9: Influence of mixing intensity of dry mortar on water repellence

100% (measured in the laboratory) water repellence of premixed plaster is achieved with 0.5 % zinc stearate at a mixing time of 200 seconds. In comparison only 70% are water repellent at 1 minute mixing time. In practice that means that often the water repellent agents are not fully effective or the batches are not mixed homogenously.

4.7 Long-time effect of the metal soaps

The surface of water-repellent plasters shows a clear drip-off effect of the water at the surface. Often this effect is lost after years. This shows that the hydrophobicity decreases over time. A possible explanation is the influence of the UV-radiation. This perception must be contradicted even from theoretical considerations.

Fatty acids can only be oxidized by UV radiation. But even this new derivate exhibits a hydrophobic behaviour. Apart from that the total plaster section is made water repellent. The UV-radiations act, however, only on the surface and not affect the deeper layers of the building materials. Chemically, metal soaps are inert and stable in the alkaline medium of plasters. Investigations have shown that the missing repellent effect at the surface of the plaster is founded by dust formation on the surface. If these are cleaned mechanically, the required drip-off effect normally recovers. As shown in Figure 10, a reduction in the water repellence can hardly be seen over years[5].

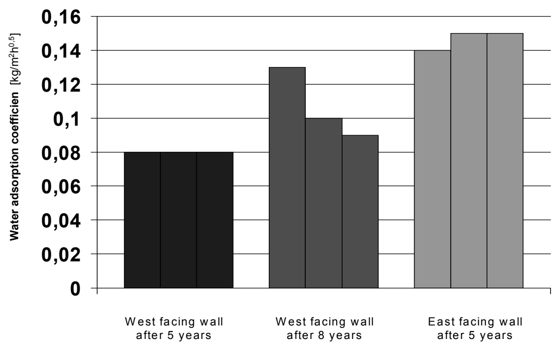


Figure 10: Long-time stability of the water repellent treatment by metal soaps.

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