SINTEF Building and Infrastructure   Harald Justnes
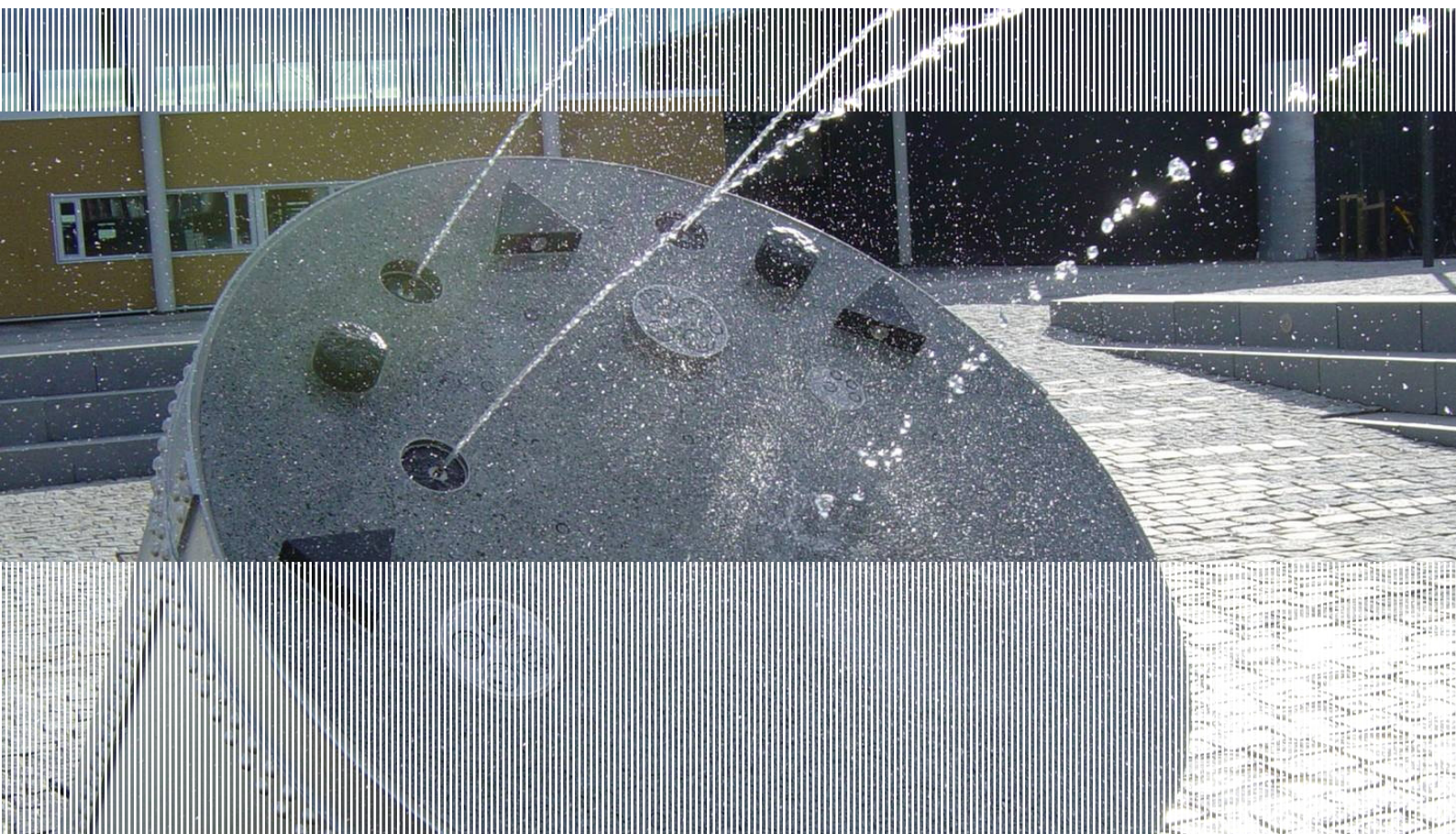
Low water permeability through hydrophobicity

COIN Project report 1 - 2008

SINTEF

SINTEF Building and Infrastructure

Harald Justnes

Low water permeability through hydrophobicity

COIN Project P1 advanced cementing materials

SP 1.5 F Low porosity / permeability

COIN Project report 1 – 2008

Cooperation partners / Consortium Concrete Innovation Centre (COIN)

Summary

The durability and aesthetic appearance of concrete may be improved by the addition of hydrophobizing agents as a consequence of reduced water permeability.

Hydrophobizing agents lead to less water absorption at the same time as they let water vapour out. This may lead to a dryer interior over time and thereby reduced rate of detrimental reactions needing liquid water as reaction medium. The ingress of water born aggressives like chlorides will be reduced (in particular in marine splash zones), but also corrosion rates may be decreased. Carbonation rates may, however, be somewhat increased.

Vegetable oils seem to be the most cost-effective hydrophobizing agents as good effects may be achieved by additions of only 0.5 % of the cement mass. Furthermore, the cheapest and most available vegetable oil based on rapeseed is among the most effective tested.

It is recommende to continue research on the effect of rapeseed oil as a concrete admixture, also at dosages above 1.5 %. The research should focus on rapeseed oil as hydrophobizing agent, but also on its effect on other interesting concrete properties for COIN; like hardening retarder, shrinkage reducing agents, electrical resistivity and pH reduction.

Oslo, 2008

Tor Arne Hammer   Harald Justnes
Centre Manager

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.coinweb.no

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1 INTRODUCTION

Hydrophobizing agents for concrete (sometimes called concrete dampproofers) are integral admixtures that modify the concrete surface so that it becomes water repellent, or less "wettable". This is illustrated in Fig.1 which shows a drop of water on the surface of a concrete that has had a hydrophobizing agent incorporated into it.
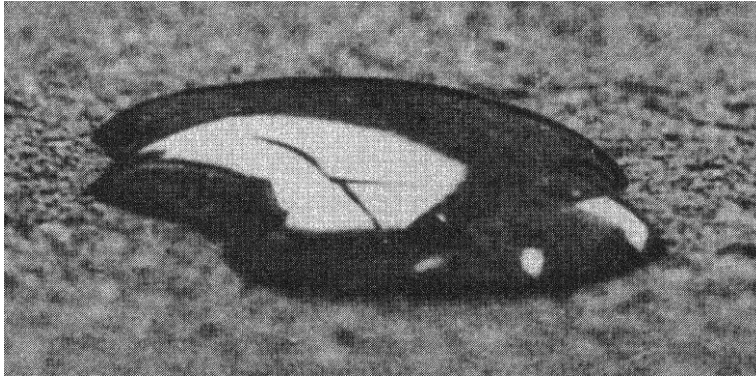
Fig. 1 A water droplet on concrete with hydrophobizing admixture showing a low degree of wetting (Rixom and Mailvaganam, 1999).

This water repellency conferred on the concrete is only effective in preventing water from entering the surface when the applied pressure is small, like rainfall in windy conditions or capillary rise. The latter effect is shown in Fig.2.
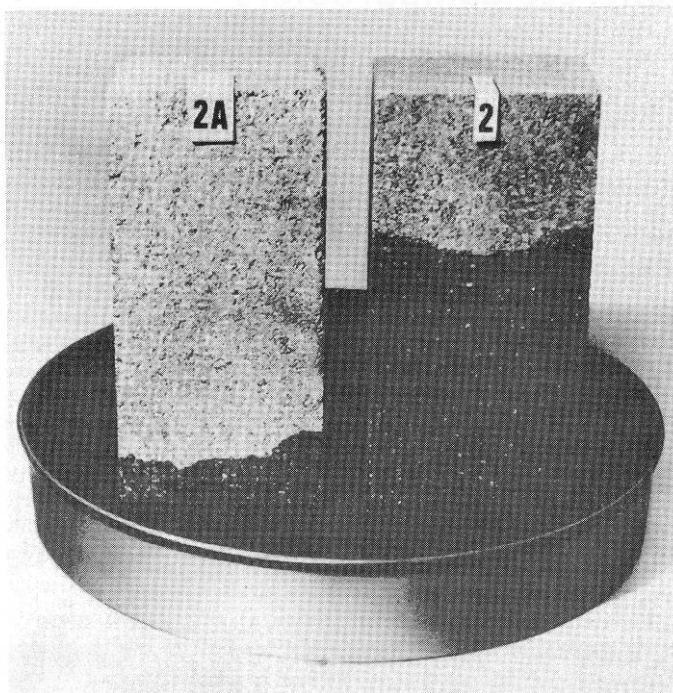
Fig. 2 Capillary rise in concrete with hydrophobizing agent (labelled 2A) showing almost no capillary rise in contrast to concrete without such an admixture (labelled 2). The picture is reproduced from Rixom and Mailvaganam (1999).

In view of this, these admixtures are normally used for improving the quality of concrete pavers, tiles, bricks, blocks and cladding panels where the additional benefits of reduced efflorescence, easier maintenance of clean surfaces and more even drying out of adjacent bricks and panels are obtained. Thus, hydrophobizing agents may contribute to the overall goal of COIN; "attractive concrete" in its aesthetical sense.

Concrete with hydrophobizing agents should also be more resistant to intrusion of water born aggressives, such as chlorides from sea water in the splash zone. Furthermore, the interior will dry out over time if the concrete loose more water by evaporation than it takes up by capillary absorption. Since most detrimental chemical reactions in concrete is dependent on liquid water, such processes may halt or be delayed. Thus, improved durability of concrete with hydrophobizing agents is to be expected.

2 OBJECTIVE

The objective of this STAR is to make a review of the possibility of achieving low water permeability of concrete through hydrophobicity. This is best realized by adding a hydrophobizing agent to the fresh concrete mix, although hydrophobicity also may be achieved for existing concrete structures by applying liquid hydrophobizing agents to their surfaces. The focus of this report is on addition of hydrophobizing admixtures to fresh concrete.

3 PRINCIPLES

Hardened Portland cement contains a distribution of pore sizes depending on the initial water-to-cement ratio (w/c) and the degree of cement hydration. The majority of pores in ordinary concrete have diameters in the range 0.05-1.0 μm and it is through these pores the water passes by applied pressure or capillary rise. It is believed that in the presence of hydrophobizing admixtures, the surfaces of the pores become coated either with a layer of molecules (e.g. in the case of fatty acids) or a layer of coalesced or separate particles (e.g. in the case of wax emulsions or latices) as illustrated in Fig. 3. The end result in both cases is the production of hydrophobic surfaces exhibiting high contact angels to water as shown in Fig. 4.
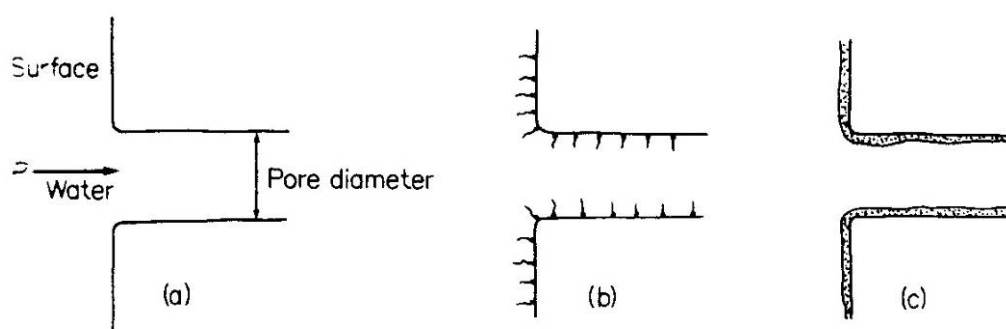
Fig. 3 Capillary pore without hydrophobizing agent (a), lined with molecular hydrophobizing agent (b) and lined with a coalesced emulsion layer (c) after Rixom and Mailvaganam (1999).

The pressure P required to force water into a pore of radius r is given by the expression

$$P = -2 \cdot \gamma \cdot \cos\theta / r \qquad\qquad\qquad [1]$$

where γ is the surface tension of water (72 dyn·cm^{-1} or 0.072 N·m^{-1}) and θ is the contact angle of water (about 120° for surfaces coated with waxes or fatty acids). For a pore with radius 0.5 μm (largest capillary), the required pressure becomes to an equivalent of a hydrostatic head of 14 m water.
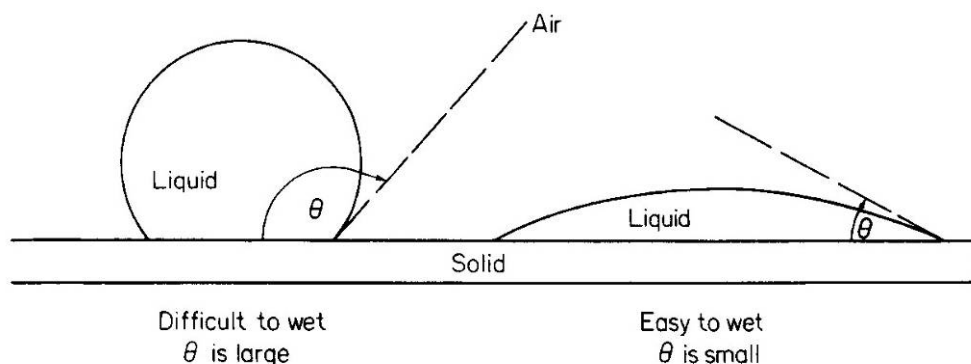
Fig. 4 Illustration of water drops on surfaces with high (left) and low (right) contact angles (θ) after Rixom and Mailvaganam (1999).

The effect of the high water contact angle surface is in theory two-fold:
1. The pressure required for water to enter the surface is positive, and therefore capillary rise should not occur. However, due to incomplete coating there will be some water absorption, but this will be considerably reduced in comparison to an untreated concrete.
2. The approximate requirement of a 14 m head of water to penetrate the surface of concrete with a good hydrophobizing agent can be related to the pressure exerted by the impact of the average rain drop (e.g. 0.5 g in mass) in various wind speeds (Wakenham, 1945). Wind speeds of 10, 20, 40, 60, 80, 100 and 120 km/h means a rain drop pressure of 140, 280, 560, 840, 1,120, 1,400 and 1,680 cm head of water, respectively.

Concrete with hydrophobizing admixtures should therefore not show significant uptake of surface water in conditions of rain and wind up with speed up to about 100 km/h (or 28 m/s = Storm). In fact, on prolonged exposure, some wetting does occur, because of defects in the hydrophobizing coating and the presence of larger voids in concrete due to incomplete compaction etc.

4 TYPES OF HYDROPHOBIZING AGENTS

4.1 General
The chemicals used to produce hydrophobizing agents are able to form a thin hydrophobic layer within the pores and voids and on the surfaces of concrete in one of 3 ways; 1) reaction with hydration products, 2) coalescence from globular particles form (i.e. emulsions) and 3) distribution in the concrete matrix in a very finely divided form. Chemicals used in each of the three categories are exemplified in Table 1 (Rixom and Mailvaganam, 1999).

Table 1 Examples of chemicals used as hydrophobizing agents for concrete

Mechanism	Chemical	Reference
Reaction with cement hydration products	Stearic acid, $C_{17}H_{35}COOH$ Oleic acid, $C_{17}H_{33}COOH$ Vegetable and animal fats Butyl stearate (ester) Caprylic, $C_7H_{15}COOH$, and Capric, $C_9H_{19}COOH$, acids	Nurie (1953) Australian patent (1964) Anon (1965) British patent (1976)
Coalescence from emulsion	Wax emulsions	Australian patent (1964) Anon (1970)
Finely divided material	Calcium stearate Aluminium stearate Bitumen	Lea (1956), Anon (1965) Dennis (1970) Dennis (1970)

4.2 Fatty acids or their salts

Fatty acids added to cementitious materials will rather quickly be neutralized by calcium hydroxide (see Eq. 2) and the hydrophilic end of the molecule, the acid group, will coordinate strongly to calcium at any surface. Thus, the hydrophobic part of the fatty acid, the alkyl or alkenyl group will poke away from the surface and ensure a high contact angle towards water.

$$2\ RCOOH + Ca(OH)_2 = 2\ H_2O + 2\ RCOO^- + Ca^{2+} \tag{2}$$
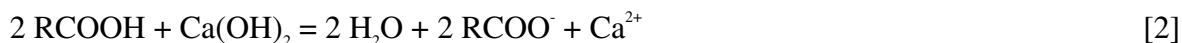
Fatty acid salts added as hydrophobizing agents are fatty acids that already are neutralized.

Saturated (i.e. no double bonds) fatty acids have the general formula $C_nH_{(2n+1)}COOH$, while fatty acids with one or two double bonds have general formulas $C_nH_{(2n-1)}COOH$ and $C_nH_{(2n-3)}COOH$, respectively. Saturated fatty acids seem to be preferred as hydrophobizing agents.

Hydrophobizing agents based on *liquid* fatty acids, such as oleic, caprylic and capric acids, are added directly to the concrete mix without predilution or added to the gauging water. A typical example of such an admixture (British patent, 1976) consisted of 1.1 % $C_5H_{11}COOH$ (caproic acid), 73.3 % $C_7H_{15}COOH$ (caprylic acid), 21.5 % $C_9H_{19}COOH$ (capric acid) and 4.3 % $C_{11}H_{23}COOH$ (lauric acid).

The *solid* fatty acid, stearic acid, is widely used as a hydrophobizing agent and can be added directly to the concrete mix in powder form, premixed with inert filler, such as talc or silica that aids dispersion throughout the mix, or as for the same reason, as an emulsion in water.

The finely divided hydrophobic salts calcium and aluminium stearate are widely used in the concrete product industry. Calcium stearate can be produced by grinding stearic acid with lime or cement to produce a material containing 10-30 % calcium stearate.

4.3 Vegetable oils, animal fat and esters

Natural fats, as vegetable oils are, consist primarily of **glycerides** (i.e. esters of glycerol and fatty acids) but also other lipids in minor quantities. Because of their preponderant weight in the glyceride molecules and also because they comprise the reactive portion of the molecules, the **fatty acids** influence greatly both the physical and chemical character of glycerides. Most oils and fats are based on about a dozen fatty acids. It is important to distinguish between the **saturated acids**, and **unsaturated acids** (see Table 2).

Table 2 Common saturated and unsaturated fatty acids.

Lauric acid	$CH_3(CH_2)_{10}COOH$	(12:0)	saturated fatty acid with 12 carbon atoms (C)
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	(18:1)	unsaturated fatty acid with 1 double bond and 18 C
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	(18:2)	unsaturated fatty acid with 2 double bonds and 18 C
Linolenic acid	$CH_3CH_2CH=CHCH_2CH=CHCH_2-CH=CH(CH_2)_7COOH$	(18:3)	unsaturated fatty acid with 3 double bonds and 18 C
Arachidonic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2-CH=CHCH_2CH=CH(CH_2)_3COOH$	(20:4)	unsaturated fatty acid with 4 double bonds and 20 C

The difference between the vegetable oils is that saturated ones contain only single bonds between carbon atoms in their fatty acids, such as *palmitic* (17:0) or *stearic* (18:0), and are characterized by relatively high melting temperatures, while unsaturated acids have one or more pairs of carbon atoms joined by double bonds, such as *oleic* (18:1) or *linoleic* (18:2), and are low melting and chemically much more reactive. The numbers in brackets are the total number of carbon atoms followed by the number of double bonds.

Glyceride (like other esters) is not chemically stable in the highly alkaline interior of a cement mortar. It will hydrolyze to glycerol, $CH(OH)CH(OH)CH(OH)$, and fatty acid anions consuming three hydroxyl ions in the process. The carboxyl group, $-COO^-$, of the fatty acid anion will coordinate strongly with calcium. The fatty acid will thus be stuck inside the mortar and the hydrophobic part of the molecule will create water repellency.

Justnes et al. (2004) tested the following 7 vegetable oils as hydrophobizing agents; Sunflower, Olive, Soya, Peanut, Linseed, Corn and Rapeseed (all food quality, except linseed oil, in these experiments, but less pure oil can probably be used with similar effect). Their distribution of fatty acid classes unsaturated, mono- and poly-unsaturated are summarized in Table 3 as stated on the bottles, while their specific fatty acids from a general view can be seen in Table 4 as found in literature (Gunstone, 1996). The oils were simply dispersed in the water with the aid of lignosulphonate plasticizer immediately prior to mixing with the mortar.

Table 3 Distribution of classes of fatty acids in some vegetable oils.

Oil type	Saturated	Monounsaturated	Polyunsaturated
Sunflower	11	21	64
Olive	15	70	15
Soya	16	19	65
Peanut	18	46	28
Corn	14	≈ 33	53
Rapeseed	5	58	32

Table 4 General distribution (%) of specific fatty acids in vegetable oils (Gunstone, 1996)

Oil type	16:0	18:0	18:1	18:2	18:3	Other
Sunflower	6	5	20	69	trace	-
Olive	10	2	78	7	1	2
Soya	11	4	22	53	8	2
Ground nut	13	3	38	41	trace	5 C_{20-24}
Linseed	6	3	17	14	60	-
Corn	13	3	31	52	1	-
Rapeseed	4	2	56	26	10	2 20:1

Certain vegetable and animal fats have been used as dampproofers and emulsions or pastes are preferred with typical compositions given in Table 5 (Dory, 1969). The fat can be white grease, tallow or soya bean oil and although they all produce hydrophobic concrete, different effects on compressive strength is obtained.

Table 5 Typical composition (%) of fat-based dampproofers (Dory, 1969)

Component in	Emulsion	Paste
Finely divided silica	11.2	30.0
Calcium hydroxide	2.0	5.0
Anhydrous calcium chloride	2.2	10.0
Calcium carbonate	1.0	1.0
Fat	2.0	20.0
Water	75.0	20.0
Mineral spirit	-	10.0

The liquid (melting point about 19°C) butyl stearate is an ester (general formula RC(O)OR' where R and R' are same or different organic groups) and is usually added as an emulsion since it is immiscible with water. It is claimed to disperse better throughout the mix compared to stearic acid, so that less material is required (Anon, 1965). Like the fats, butyl stearate will also undergo alkaline hydrolysis in the concrete, in this case to stearate and butanol;

$$CH_3(CH_2)_{16}C(O)O(CH_2)_3CH_3 + OH^- = CH_3(CH_2)_{16}COO^- + CH_3(CH_2)_3OH \qquad [3]$$
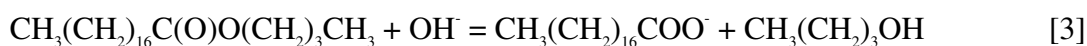
4.4 Wax and polymer emulsions

Very finely divided wax emulsions are effective concrete hydrophobizing agents and are formulated so that the emulsion breaks down after contact with the alkaline pore water of concrete and form a hydrophobic layer after coalescence. Waxes of melting point 57-60°C are used with an emulsifying agent based on sorbitan monostearate or ethoxylated sorbitan monostearate (Australian patent, 1964). The emulsifying agents may be classified as esters and they will hydrolyse in an analogue manner to butyl stearate outlined in Eq. 3. The properties of a commercial wax emulsion are listed in Table 6 (Anon, 1970).

Table 6 Typical characteristics of wax emulsion type hydrophobizing agent (Anon, 1970)

Appearance	Milky white emulsion
Specific gravity (kg/litre)	0.98
pH	6.5 - 7.0
Viscosity (cP)	6 - 8
Size of wax particle (µm)	0.5 - 1.0
Solids content (%)	30

Latex (latices in plural) is an emulsion of synthetic polymers of various types. Latices may also be dried to redispersible powders for pre-packed mortars. The major use of latices and redispersible powders are for repair mortars and overlays probably because of the cost. Latices are relative expensive and a dosage in the order of 5 % polymer is required to get particular benefits. Latices are often used to improve adhesion between new and old concrete, in which they are rather cost-effective. Justnes (2007) recently reviewed the principles and performance of latex modified mortars and discussed the primary properties of the polymer; 1) the minimum film forming temperature (MFT) of the polymer, 2) the polymer toughness, 3) polymer particle distribution, 4) polymer stability against alkaline hydrolysis and 5) surfactants. Secondary effects on the mortar were also discussed namely; 1) air entrapment, 2) workability, 3) retardation of cement hydration and 4) water content in pores. Latices are also believed to coalesce to a continuous film if the MFT is lower than ambient temperature, but they will form a stronger network than waxes. The polymer network in a mortar added 10 % polymer of cement mass as latex is exposed after removing cement by acid etching in Fig. 5 (Justnes, 2007).

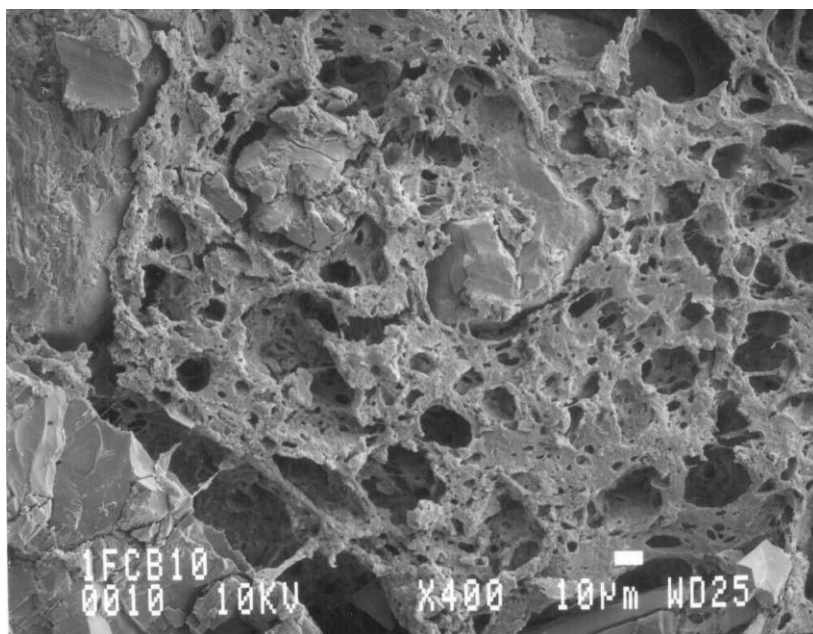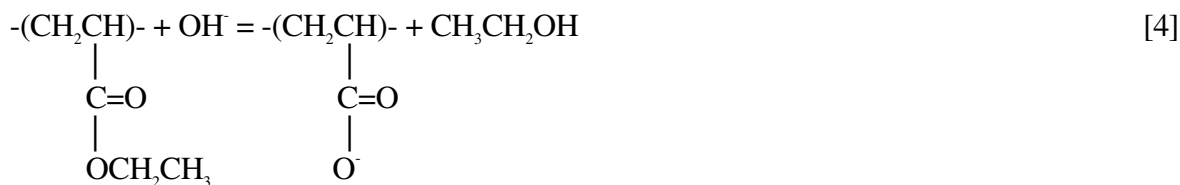Fig. 5   SEM image of etched PCC with 10 % polymer (MFT = 12°C) after 28 days hydration at 20°C showing a "chewing gum" like polymer network (Justnes, 2007).

Note that some polymers are not stable in the alkaline pore water of concrete and may degrade over time. Both lower acrylics like polyethyl acrylate (Eq. 4) and polyvinyl acetates (Eq. 5) may hydrolyse consuming OH$^-$ and producing ethanol or acetate ions, respectively:

$$-(CH_2CH)- + OH^- = -(CH_2CH)- + CH_3CH_2OH \qquad\qquad [4]$$

<div style="padding-left:2em">
|
C=O   C=O
| |
OCH_2CH_3   O^-
</div>

$$-(CH_2CH)- + OH^- = -(CH_2CH)- + CH_3CH_2COO^- \qquad\qquad [5]$$

<div style="padding-left:2em">
| |
O   OH
|
O=CH_2CH_3
</div>

Lu et al. (2004) improved the water repellence and lowered the permeability of mortar by adding a complex admixture based on a water soluble polymer (i.e. polyacrylamide) and a superplasticizer (i.e. naphthalenesulphonate - formaldehyde condensate).

4.5 Silanes

Silane is a chemical compound, SiH_4, named in analogy to methane, CH_4. Further in analogy to organic compounds based on carbon, a number of functional organic groups can substitute the hydrogen and form covalent bonds to silicon. In the field of hydrophobizing agents it is common to quote silanes with the general formula $RSi(OR')_3$ where R is a long or bulky alkyl group and R' is a relatively short alkyl group. Like ethyl since it should be hydrolysed by the hydroxides from the cement in order for it to coordinate to calcium (just like the $-COO^-$ group in fatty acid salts) and the R group poke out from the surface and is responsible for the hydrophobizing action;

$$RSi(OR')_3 + 3\ OH^- = RSi(O^-)_3 + 3\ R'OH \qquad\qquad [6]$$

Or

$$RSi(OR')_3 + 3\ H_2O = RSi(OH)_3 + 3\ R'OH \qquad\qquad [7]$$

The pH of the water in the concrete mix determines if the silicon is terminated with -OH (Eq. 7) or $-O^-$ groups (Eq. 6). It might actually be a blend of both.

Silanes are often used as hydrophobizing agents applied to the surface of existing concrete structures, but seldom used as additive to fresh concrete. Whether this is a question of cost, as they are much more expensive than fats or fatty acids, or retardation of the cement hydration, as they may coordinate strongly to cement grains, are not known. Any retardation may be minimized by delaying Eq. 6 and 7 by increasing the length of the alkyl group R'.

Xu and Chung (2000) used silanes to improve the workability of mortars with silica fume. They either pre-treated silica fume with a complex silane mixture or added silane to the mortar mix together with silica fume. Unfortunately they did not measure the water absorption of hardened mortar, only mechanical properties.

4.6 Siloxanes

A siloxane is any chemical compound composed of units of the form R_2SiO, where R is a hydrogen atom or a hydrocarbon group. A siloxane has a branched or unbranched backbone of alternating silicon and oxygen atoms -Si-O-Si-O-, with side chains R attached to the silicon atoms. As a hydrophobizing agent it is designed in analogy to silanes, with the exception of the

"polymerization" -Si-O-Si-O-. The names silane and siloxane is often incorrectly used for each other.

5   PERFORMANCE TESTING OF HYDROPHOBIZING AGENTS

Performance testing of hydrophobizing agents on hardened concrete and mortars is most easily done by capillary suction tests of water by a simple weighing procedure as outlined in the proceeding text. Permeability tests where pressurized water is applied and the water penetration measured is more difficult to perform (i.e. due the requirement of a complex rig). Martys and Ferraris (1997) reviewed the capillary transport in mortars and concrete.

The weighing procedure for a capillary suction test consists of 6 important steps for the specimen:
1. Drying to constant weight (W_1)
2. Capillary suction for 5 days with weight monitoring
3. Water saturation by submersion 3 days in water at 1 atm (W_2)
4. Pressure saturation by submersion 3 days in water at 80 atm (W_3)
5. The outer volume (V) is recorded by differential weighing the specimen under water and saturated surface dry in air according to the principle of Archimedes.
6. Drying the specimen to constant weight at 105°C (W_4)

From these 6 steps, one can calculate the initial moisture content, total porosity (ε_{tot}), the capillary porosity (ε_{cap}), the air volume (ε_{air}), the average density of the concrete solids (ρ_{sol}) and the dry density of the concrete (ρ_{dry}) according to the following formulas;

$$Initial \quad moisture = \frac{(W_1 - W_4) \cdot 100\%}{V \cdot \rho_w} \qquad \text{[vol\%]} \qquad \text{[8]}$$

$$\varepsilon_{tot} = \frac{(W_3 - W_1) \cdot 100\%}{V \cdot \rho_w} \qquad \text{[vol\%]} \qquad \text{[9]}$$

$$\varepsilon_{cap} = \frac{(W_2 - W_1) \cdot 100\%}{V \cdot \rho_w} \qquad \text{[vol\%]} \qquad \text{[10]}$$

$$\varepsilon_{air} = \frac{(W_3 - W_2) \cdot 100\%}{V \cdot \rho_w} \qquad \text{[vol\%]} \qquad \text{[11]}$$

$$\rho_{sol} = \frac{W_1}{V - \frac{(W_3 - W_1)}{\rho_w}} = \frac{W_1}{V \cdot \left(1 - \frac{\varepsilon_{tot}}{100\%}\right)} \qquad \text{[kg/m}^3\text{]} \qquad \text{[12]}$$

$$\rho_{dry} = \frac{W_1}{V} \qquad \text{[kg/m}^3\text{]} \qquad \text{[13]}$$

It is recommended to test the water vapour diffusion of mortar and concrete when hydrophobizing agents are added. This is because the ideal performance is to block liquid water from entering and let water vapour out easily. Thereby the water saturation of the capillary pores may be lowered and the reaction rate of most detrimental reactions halt since liquid water usually is required as reaction medium.

The water vapour diffusion test can easily be done by mounting mortar or concrete slices on a metal cup with a wet sponge in the bottom. This test unit can be placed in a room of 50 % RH so the driving force for vapour diffusion will be the difference between this vapour concentration and 93 %

RH inside the cup obtained by potassium nitrate saturated water. Usually three parallels are made for each mortar or concrete type. The diffusion coefficient is calculated from Eq. 14 where dS indicates the amount of water vapour diffused through a cross-section A per unit time, dt, and ΔC symbolizes the concentration difference over the thickness ℓ. dS/dt is the slope of the linear weight loss of the test unit versus time plots. The mass of the test unit should be measured every 2 or 3 days until the 4 last data used in a linear regression analysis to determine the slope give a regression factor $r^2 > 0.98$ in order to secure a steady state condition.

$$\frac{dS}{dt} = -D_{eff} \cdot A \cdot \frac{\Delta C}{\ell}$$
[14]

Justnes et al. (2004) tested 7 vegetable oils as hydrophobizing agents both with respect to capillary suction and water vapour diffusion: Standard mortars were composed of ordinary Portland cement, 0-8 mm sand, lime stone filler (20 % of cement weight), water and 0.3 % plasticizer (40 % solution of sodium lignosulphonate) of cement weight as a dispersant for the oil. The w/c was 0.50, and the cement:sand ratio was 1:3. Vegetable oil was dispersed in water with lignosulphonate for one minute before adding it to the dry materials. Then all ingredients were mixed for one minute in a Hobart mixer, 1 min resting and 1 min remixing. 20 mm slices were cut from 100·200 mm cylinders after 28 days curing and dried for one week at 50°C (instead of the usual 105°C) in order not to alter the vegetable oil. The parameters derived from the capillary suction test; initial moisture, capillary porosity, entrained air, solid density and dry density, are listed in the case of cast discs for all 23 mixtures in Table 7 and for sawn discs in Table 8. The water absorption versus square root of time profiles for mortars with rapeseed oil is plotted in Fig. 6.

The first to be noticed from Tables 7 and 8 is that the air content (ε_{air}) seems to increase with increasing oil addition. This is not the case, but rather the oil reducing the water absorption so much that even 4 days suction followed by 2 days water submerging is not sufficient to fill all the capillaries. Thus, when the samples are placed in the pressure tank, the unfilled capillaries will be saturated and erroneously be interpreted as air. Summing up initial moisture, capillary moisture and entrained air should then give the correct total porosity. This is done in Table 13 and is rather constant for all mixtures, indicating that the total air content does not vary too much between the mixtures. Thus, the "apparent air content" can be a good measure of the resistance to capillary suction and used to rank the efficiency of vegetable oils:

Cast disc, 0.5% addition: Rapeseed > olive ≈ peanut ≈ corn > linseed > soya > sunflower
Cast disc, 1.0% addition: Olive > rapeseed = peanut = corn > linseed > soya > sunflower
Cast disc, 1.5% addition: Peanut > olive ≈ rapeseed > linseed > corn > soya = sunflower
Sawn disc, 0.5% addition: Olive > linseed ≈ rapeseed > corn ≈ peanut > soya > sunflower
Sawn disc, 1.0% addition: Olive > peanut > rapeseed > linseed ≈ corn > soya ≈ sunflower
Sawn disc, 1.5% addition: Peanut ≈ olive > rapeseed > corn ≈ soya > linseed ≈ sunflower

Even though the ranking seems to shift somewhat depending on dosage and whether the discs were cast or sawn, the three oils; olive, rapeseed and peanut, seem to give the best water repellence. As seen from Tables 3 and 4, these are also the oils with the most monounsaturated fatty acids. The content of polyunsaturated fat does not seem to play a role, as soya and sunflower overall do not perform as well.
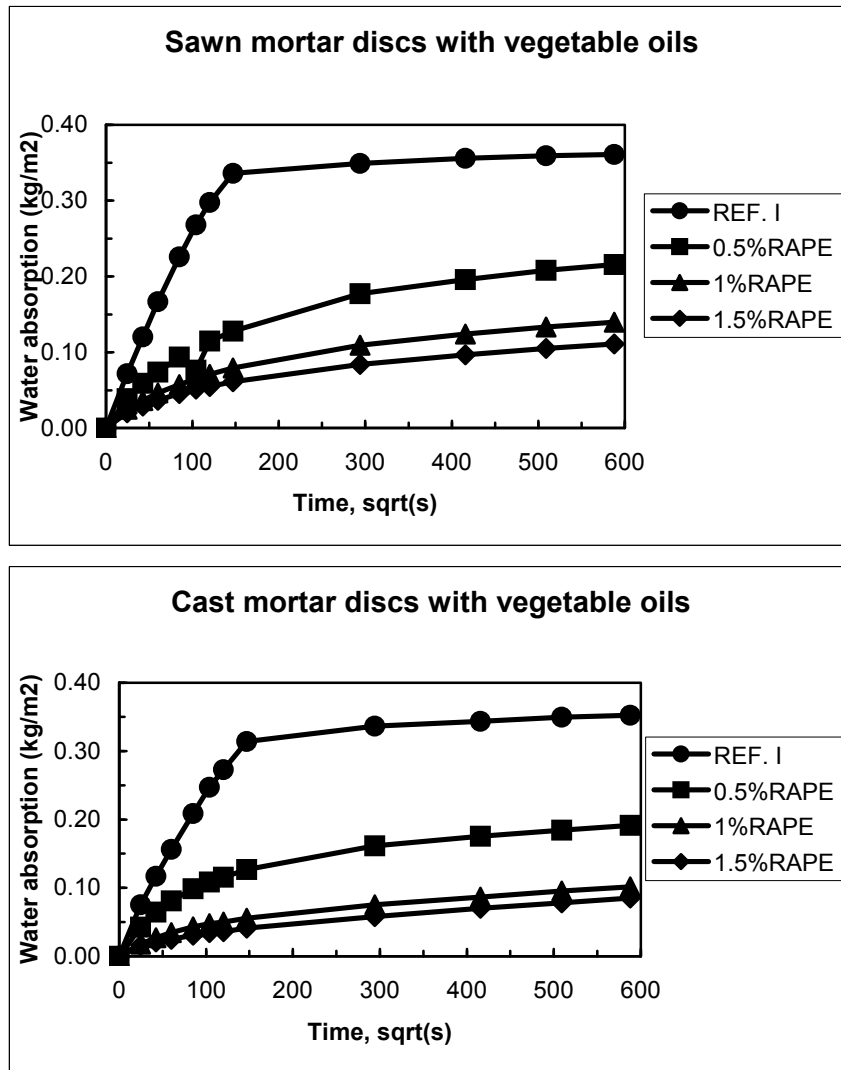
Fig. 6 Water absorption of sawn (upper) and cast (lower) discs of mortars with 0.0, 0.5, 1.0 and 1.5 % rapeseed oil added. Note that the y-axes are wrong with a factor of 10, so that 0.40 kg/m^2 really should be 4.0 kg/m^2 and so on.

The effective diffusion coefficients, D_{eff}, and the correlation factor, r^2, from the linear regression analysis of the average mass loss versus time curve (dS/dt in Eq. 14 is the slope of the mass loss versus time curve) of three specimens are listed in Table 9 for both sawn (indicate interior water movement) and cast discs (includes effect of surface skin) of mortars with the 7 different vegetable oils tested by Justnes et al. (2004).

The results in Table 9 show clearly that the vapor diffusion through the mortar is dominated by the surface skin of cement paste as seen from the difference between sawn and cast reference mortar (63 % reduction). The oil addition do not lower the vapor diffusion coefficient further for cast specimen, but reduces it relative to the reference for the sawn specimen, sometimes to the level of the cast specimen. The latter effect indicates that there can be some pore blocking by remaining oil droplets, but they may be degraded by alkaline moisture over time. The samples were 2-3 months old at the time of measurement.

Table 7 Initial moisture, capillary porosity, ε_{cap}, air content, ε_{air}, average density of solids, ρ_s, and dry sample density, ρ_d, obtained by the capillary suction technique for <u>cast</u> discs of mortars with different vegetable oil additions (Justnes et al., 2004).

Oil Type	Dose (%)	Initial moist (%)	ε_{cap} (vol%)	ε_{air} (vol%)	ρ_s (kg/m^3)	ρ_d (kg/m^3)
None	0	2.1±0.1	13.5+0.1	2.7±0.1	2567±2	2199±3
	0	2.2±0.2	14.3±0.3	2.6±0.2	2584±1	2193±8
Sunflower	0.5	2.5±0.1	13.2±0.1	2.7±0.0	2556±9	2194±11
	1.0	3.5±0.0	10.5±0.5	4.5±0.7	2478±19	2182±4
	1.5	3.4±0.1	7.9±0.6	7.5±0.9	2391±35	2168±20
Olive	0.5	3.0±0.1	9.0±0.4	6.2±0.3	2448±10	2197±17
	1.0	3.4±0.4	6.2±0.4	9.5+0.6	2335±12	2156±13
	1.5	3.3±0.1	4.7±0.1	9.9±0.3	2347±4	2203±4
Soya	0.5	2.9±0.2	11.8±0.3	4.3±0.3	2526±5	2200±12
	1.0	3.1±0.2	8.3±0.6	6.6±0.7	2435±18	2202±1
	1.5	3.2±0.1	8.2±0.1	7.5±0.5	2406±10	2176±9
Peanut	0.5	2.9±0.1	8.9±0.2	6.1±0.3	2459±9	2212±12
	1.0	3.0±0.1	7.1±0.3	8.9±0.4	2372±16	2173±10
	1.5	3.3±0.2	5.1±0.3	10.3±0.1	2311±4	2161±8
Linseed	0.5	2.8±0.1	12.4±0.3	4.8±0.3	2487±16	2122±23
	1.0	2.2±0.1	7.9±0.2	7.7±0.3	2427±10	2214±6
	1.5	2.4±0.1	7.4±0.4	9.2±0.6	2388±16	2188±12
Corn	0.5	2.4±0.0	10.1±0.3	5.9±0.7	2475±18	2200±9
	1.0	2.4±0.6	7.6±0.7	8.9±1.0	2374±42	2170±40
	1.5	3.0±0.3	6.4±0.3	8.7±0.6	2377±13	2196±7
Rapeseed	0.5	2.6+0.2	9.0±0.8	8.0±0.7	2415±28	2171±47
	1.0	2.4±0.0	6.2±0.1	8.9±0.1	2393±10	2222±10
	1.5	2.4±0.1	5.5±0.2	9.7±0.3	2364±8	2209±5

Justnes et al. (2004) concluded that

1. Vegetable oils can be used as water repellents for mortars in rather small amounts (0.5-1.5 % of cement weight), in particular if a good distribution is secured by dispersing the oil in the mixing water prior to blending.
2. Oils with high content of monounsaturated fatty acids seem to be most effective; like olive, peanut and rapeseed. Considering the worlds production of different oils and performance, oil from rapeseeds seems to be most attractive from a concrete technology perspective, in particular since it easily can be grown also in colder climates.
3. At the same time as the 4 day water absorption is reduced by more than 1/3 by 1 % rapeseed oil, the water vapor diffusion coefficient in the interior is not reduced more than to the level of the cement paste skin of the reference mortar. Thus, a mortar with vegetable oil exposed to weather should develop a drier interior over time and the penetration of water born aggressives like chlorides should be reduced. For these reasons, mortar or concrete with vegetable oil addition should be more durable than without.

Table 8 Initial moisture, capillary porosity, ε_{cap}, and air content, ε_{air}, average density of solids, ρ_s, and dry sample density, ρ_d, obtained by the capillary suction technique for <u>sawn</u> discs of mortars with different vegetable oil additions (Justnes et al., 2004).

Oil Type	Dose (%)	Initial moist (%)	ε_{cap} (vol%)	ε_{air} (vol%)	ρ_s (kg/m^3)	ρ_d (kg/m^3)
None	0	2.4±0.1	14.8±0.8	2.8±0.1	2560±6	2157±25
	0	2.6±0.1	15.4±1.0	2.5±0.2	2576±5	2152±27
Sunflower	0.5	3.0±0.3	13.7±1.0	3.1±0.1	2527±5	2151+22
	1.0	3.6±0.1	12.6±1.0	3.5±0.2	2505±2	2155±22
	1.5	3.7±0.2	11.1±1.3	5.0±0.4	2442±11	2133±22
Olive	0.5	3.3±0.3	10.8±1.0	5.1±0.1	2469±9	2170±29
	1.0	3.2±0.2	8.3±0.7	8.4±0.3	2352±4	2124±15
	1.5	4.1±0.2	7.4±0.4	8.7±0.4	2357±12	2143±24
Soya	0.5	3.4+0.1	13.0±0.5	3.7±0.2	2516±11	2154±21
	1.0	3.8±0.1	11.9±1.2	3.7±0.0	2503±5	2168±33
	1.5	3.9±0.1	10.8±0.7	5.6±0.1	2445±9	2141±26
Peanut	0.5	3.4±0.0	12.0±0.9	4.3±0.2	2508±10	2172±31
	1.0	3.2±0.1	9.7±0.9	7.3±0.2	2412±2	2146±21
	1.5	3.6±0.0	7.3±0.6	8.8±0.2	2335±10	2129±23
Linseed	0.5	3.1±0.1	13.0±0.5	4.9±0.0	2474±11	2122±23
	1.0	2.9±0.1	12.7±1.1	4.8±0.1	2486±10	2141±36
	1.5	3.0±0.1	12.9±0.7	5.2±0.3	2458±8	2111±22
Corn	0.5	2.9±0.1	13.6±1.0	4.4±0.2	2500±11	2133±29
	1.0	2.9±0.1	12.6±1.1	4.6±0.1	2488±8	2146±34
	1.5	3.2±0.1	10.9±2.4	5.7±0.1	2454±28	2155±42
Rapeseed	0.5	2.9±0.0	12.1±1.3	4.8±2.2	2498±8	2166±31
	1.0	3.1±0.1	10.1±1.3	6.6±0.1	2439±7	2161±37
	1.5	3.3±0.1	8.2±0.9	8.0±0.2	2384±6	2156±23

The performance of the 7 vegetable oils as hydrophobizing agents were followed up by Vikan and Justnes (2006) after the mortars had been stored for 3 years at 20°C and 93 % RH with access to renewed air, but no sunlight. The capillary suction profiles for mortar with olive oil are plotted in Fig. 7 and the measured porosities and densities are shown in Table 10.

Justnes et al. (2004) found that the pores not available by water suction increased with increasing oil addition. They explained that this phenomenon was caused by oil droplets blocking the capillary pores. This trend was also found by Vikan and Justnes (2006) in the measurements done three years later. The values of total porosity found by Vikan and Justnes (2006) were similar to the ones Justnes et al. (2004) reported, while the share of closed macro porosity (apparent air content) increased during the three years of storage. This effect might have been caused by hydration which has made the pore structure denser. Oil droplets might furthermore block some of the capillary pores which results in high values of measured macro pores. This potential pore blocking effect is illustrated in Figs. 8 and 9. Fig. 9 illustrates further that the pore blocking ability is increasing with the amount of mono-unsaturated acids in the vegetable oils.

Table 9 Effective water vapor diffusion coefficient, D_{eff} ($10^{-6}m^2/s$), for mortars with different vegetable oil additions. The linear regression factor, r^2, is included to indicate the soundness of the fit to obtain D_{eff} (Justnes et al., 2004).

Oil type	Dosage (%)	Sawn discs		Cast discs	
		D_{eff} ($10^{-6}m^2/s$)	r^2	D_{eff} ($10^{-6}m^2/s$)	r^2
None	0	0.85	0.9946	0.31	0.9987
Sunflower	0.5	0.56	0.9807	0.29	0.9984
	1.0	0.42	0.9940	0.29	0.9879
	1.5	0.34	0.9873	0.26	0.9885
Olive	0.5	0.37	0.9989	0.28	0.9985
	1.0	0.39	0.9948	0.30	0.9931
	1.5	0.35	0.9840	0.26	0.9980
Soya	0.5	0.49	0.9859	0.35	0.9809
	1.0	0.36	0.9968	0.29	0.9981
	1.5	0.35	0.9994	0.31	0.9982
Peanut	0.5	0.40	0.9991	0.31	0.9980
	1.0	0.37	0.9988	0.33	0.9971
	1.5	0.36	0.9981	0.32	0.9967
Linseed	0.5	0.40	0.9984	0.36	0.9985
	1.0	0.38	0.9973	0.27	0.9959
	1.5	0.37	0.9968	0.29	0.9961
Corn	0.5	0.46	0.9995	0.34	0.9989
	1.0	0.38	0.9999	0.32	0.9994
	1.5	0.36	0.9997	0.31	0.9991
Rapeseed	0.5	0.47	0.9998	0.33	0.9988
	1.0	0.45	0.9984	0.34	0.9984
	1.5	-	-	0.36	0.9976

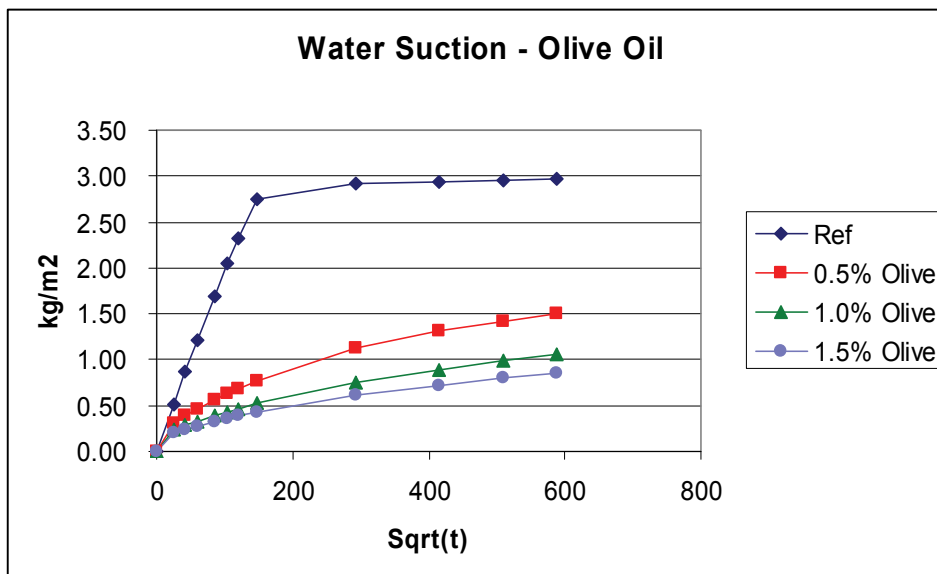

Fig. 7 Water suction measurements for mortar samples with 0-1.5 % Olive oil after 3 years moist curing. All samples have been pre-dried at 50°C. After Vikan and Justnes (2006).

Table 10 Porosities of sawn upper surface, were ε_{cap}, ε_{om}, ε_{cm}, $\Sigma\varepsilon_m$, $\Sigma\varepsilon_{tot}$ are the capillary, open macro, closed macro, sum of macro porosity and the total porosity respectively and ρ_{solid} and ρ_{dry} are the solid and dry density respectively (Vikan and Justnes, 2006).

| Oil Type	Dose (%)	ε_{cap}	ε_{om}	ε_{cm}	$\Sigma\varepsilon_m$	$\Sigma\varepsilon_{total}$	ρ_{solid}	ρ_{dry}
Ref I	0.0	17.6	0.4	2	2.4	20.0	2657	2125
Ref II	0.0	18.1	0.4	1.9	2.3	20.4	2667	2125
Corn	0.5	13.8	2.0	4.7	6.7	20.5	2653	2109
Corn	1.0	11.6	4.4	4.7	9.1	20.7	2638	2094
Corn	1.5	10.9	4.3	5.9	10.2	21.4	2896	2261
Linseed	0.5	11.6	3.7	4.6	8.3	19.9	2643	2117
Linseed	1.0	9.5	3.4	6.1	9.5	19.0	2635	2134
Linseed	1.5	9.7	2.3	7.7	10.0	19.7	2723	2180
Sunflower	0.5	12.9	3.6	3.7	7.3	20.2	2655	2120
Sunflower	1.0	12.9	3.3	3.6	6.9	19.8	2647	2122
Sunflower	1.5	11.1	4.8	4.3	9.1	20.2	2638	2105
Soya	0.5	11.7	3.2	3.9	7.1	18.8	2639	2145
Soya	1.0	11.3	3.3	4.9	8.2	19.5	2640	2124
Soya	1.5	9.4	3.0	6.4	9.4	18.8	2621	2128
Rapeseed	0.5	10.4	3.3	5.2	8.5	19.0	2630	2131
Rapeseed	1.0	8.1	2.9	7.9	10.8	18.9	2625	2128
Rapeseed	1.5	8.3	1.7	8.7	10.4	18.7	2649	2150
Peanut	0.5	11.6	3.6	3.9	7.5	19.2	2643	2136
Peanut	1.0	8.8	2.2	8.7	10.9	19.7	2609	2097
Peanut	1.5	7.1	1.9	8.8	10.7	17.8	2390	1963
Olive	0.5	9.4	3.1	5.8	8.9	18.3	2625	2144
Olive	1.0	7.8	2.2	9.3	11.5	19.4	2613	2106
Olive	1.5	7.4	2.0	8.5	10.5	17.8	2609	2143
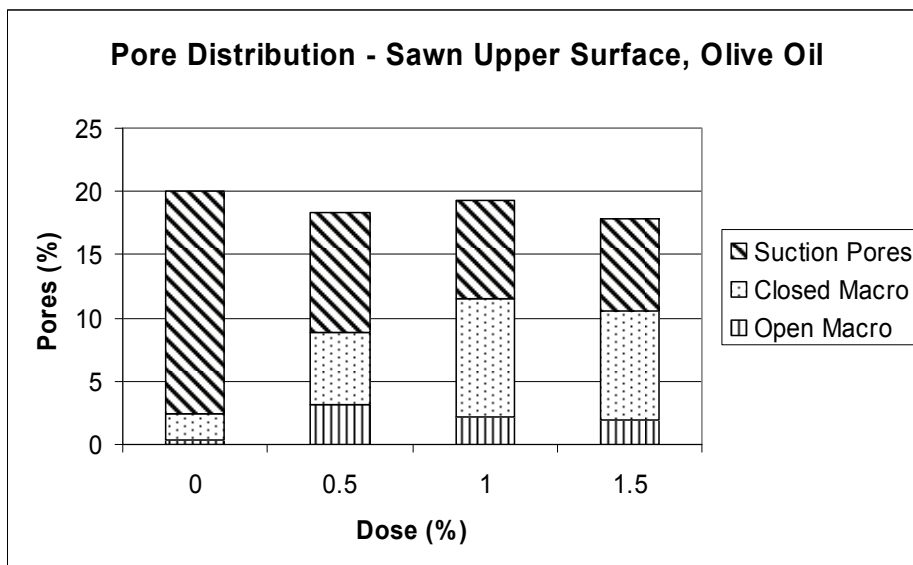
Fig. 8 Distribution of pores in mortar samples without oil and with 0.5-1.5 % olive oil. The total porosity is approximately constant for all samples, while the share of closed macro pores increases and the share of suction pores decreases with increasing oil dose (Vikan and Justnes, 2006).
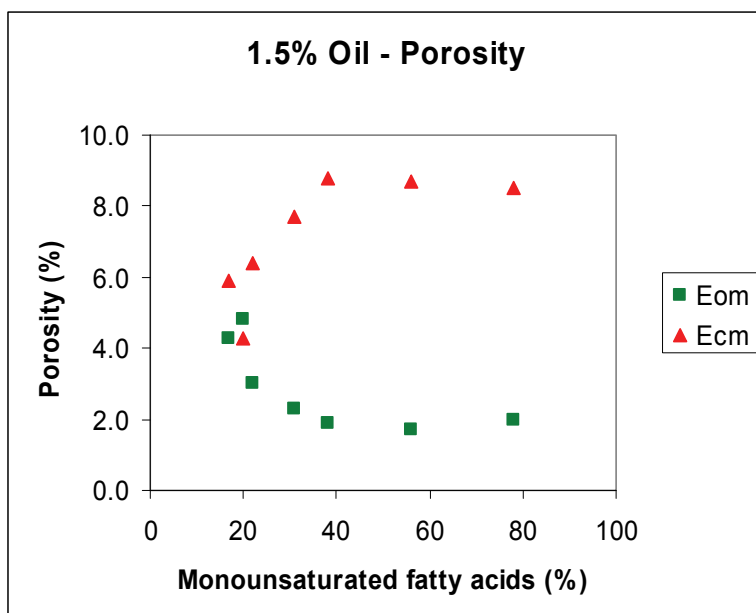
Fig. 9 Correlation between open (Eom) and closed (Ecm) macro pores and amount of mono-unsaturated acids in the oils (Vikan and Justnes, 2006).

Vikan and Justnes (2006) concluded that vegetable oils can be used as water repellents for mortars in rather small amounts (0.5-1.5 % of cement weight) and the effect last for more than 3 years at moist conditions. Oils with high content of mono-unsaturated fatty acids seem to be most effective; like olive, peanut and rapeseed. The water suction was found to be dependent on the oil concentration. The strongest effect was seen between the reference and the concentration of 0.5 % oil. Further increase of oil concentration resulted in further reduction in the water uptake, but this additional effect was not as strong.

Chandra and Xu (1995) tested linseed, corn and mustard oil, both cooked and uncooked. They tested capillary suction for 0.5 and 0.8 % additions for 2 days only. They found that the sample with 0.5 % corn oil obtained the same capillary suction value as the reference within these 2 days. From the water absorption profile of mortar with 0.5 % corn oil in the study by Justnes et al. (2004), it can be extracted that water absorption after 4 days is 0.26 kg/m^2 as compared to 0.36 kg/m^2 for the reference. At 2 days the value is 0.25 versus 0.36 kg/m^2. The difference in performance compared with Justnes et al. (2004) seems to be the lack of proper distribution of the oil by Chandra and Xu (1995), since it was added directly to the mixer rather than being dispersed in the mixing water first. Another difference is that they dried their specimen at 105°C before testing, instead of the 50°C used here. This may have destroyed some of the oil.

Justnes et al. (1998) studied the moisture transport in mortars with 0, 5, 10 and 15 % polymer of cement mass added as latices or redispersible powders. However, in this case the specimens were not dried at elevated temperatures, but simply stored at 20°C and 50 % RH to dry out. This was done not to affect the film forming of polymer with MFT higher than ambient temperature. Therefore, the capillary suction is more gradual and direct comparison with the vegetable oil specimen not fair. Nevertheless, an example of the results from the capillary suction experiment is shown in Fig. 10 for one of the best performing polymers.

The effective water vapor diffusion coefficient for the reference mortar with w/c = 0.50 obtained by Justnes et al. (2004), was a little higher (D_{eff} = 0.85·10^{-6} m^2/s) than previously measured by Justnes et al. (1998) on mortar with w/c = 0.55 (D_{eff} = 0.71·10^{-6} m^2/s). However, the RH in the cup was then 100 % in 1998 (water may then condense in capillary pores), rather than 93 % RH presenting 2004. The

reduction in D_{eff} relative to the reference by 5 % polymer addition in the form of latex (Justnes et al, 1998) was often less (depending on type) than for the addition of 1 % vegetable oil (Justnes et al., 2004).
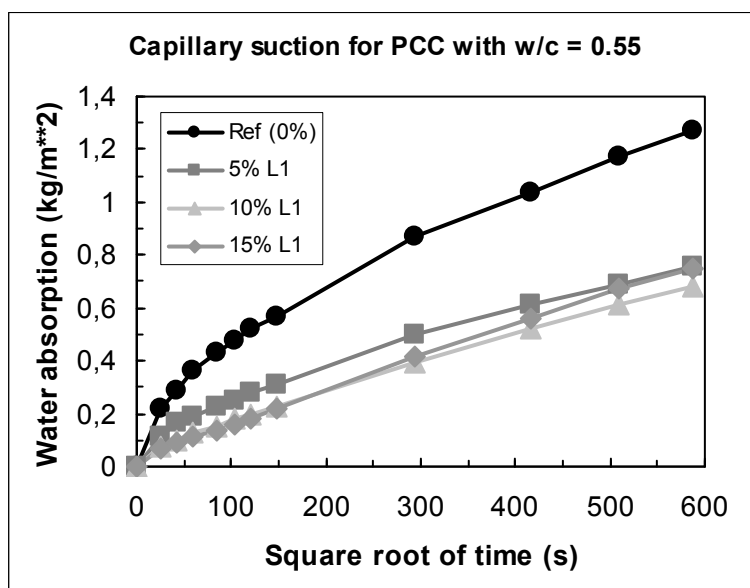

Fig. 10 Capillary suction of mortar (w/c = 0.55) modified with 0, 5, 10 and 15 % n-BA/MMA polymer as latex (Justnes et al., 1998).

Justnes et al. (1998) and Justnes and Øye (1995) performed similar capillary absorption tests for polymer latices and redispersible polymer powders. The lowest polymer dosage was 5 % of cement weight, and as a general impression even the best polymers did not perform as good as for instance 1 % rapeseed oil. On the other hand, the latices are not designed to be hydrophobizing as the primary property.

6 OTHER EFFECTS OF HYDROPHOBIZING AGENTS ON CEMENTITIOUS MATERIALS

6.1 Bleeding of cement pastes

Wax emulsions have been shown (Bruere, 1974) to cause a considerable reduction in the bleeding rates and capacities of cement pastes as illustrated in Fig. 11 in comparison to bentonite (B) and kaolin (K) additions. Although not as effective as bentonite, some of the wax emulsions are clearly very beneficial in this role.

6.2 Hydration of cement pastes

Addition of hydrophobizing agents based on caprylic, capric or stearic acids, stearates or wax emulsions do not have any effect on the setting characteristics of hydrating Portland cement. However, the unsaturated fatty acid salts, such as oleates, have a marked effect on the ettringite and monosulphate reaction, although not affecting alite hydration (Nasser, 1973). This is illustrated by rate of hydration heat from isothermal calorimetry in Fig. 12. It is possible that a calcium oleoaluminate hydrate complex is formed involving the double bond of the oleic acid.
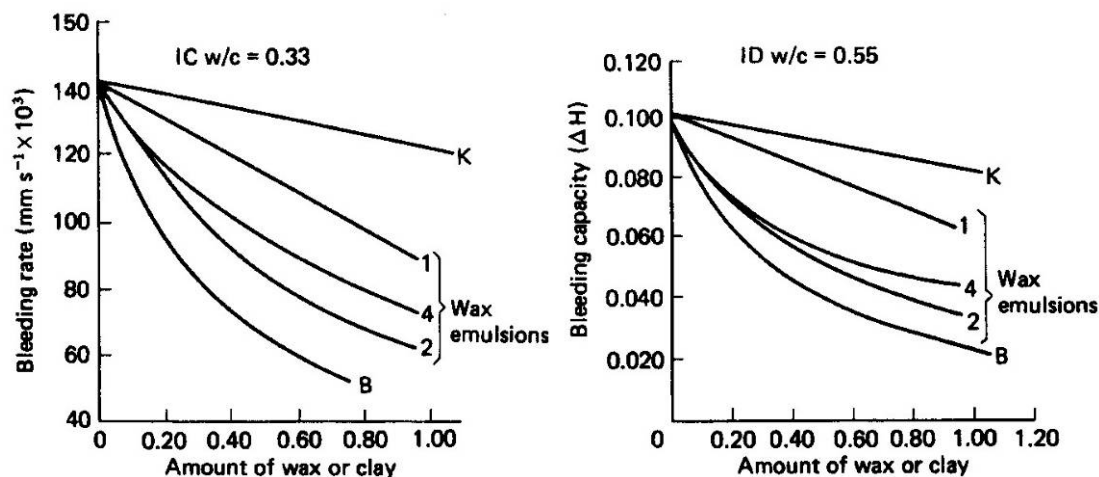
Fig. 11 The influence of wax emulsions (% wax of cement mass) on the bleeding of cement pastes (Bruere, 1974).
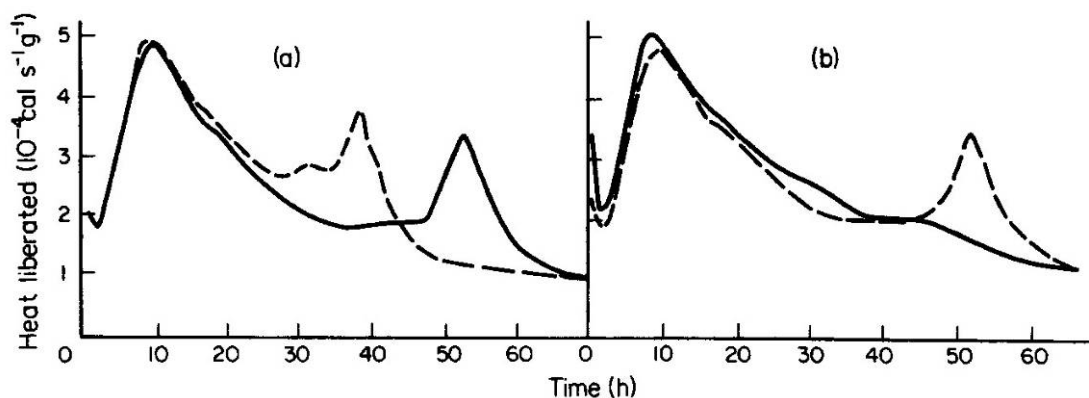

Fig. 12 The influence of sodium oleates on rate of hydration heat of two different cements (Nasser, 1973) by isothermal calorimetry. Solid line for reference and dashed with sodium oleate.

Justnes et al. (2004) used lignosulphonate plasticizer to emulsify vegetable oil rapidly in the mixing water prior to addition. The temperature evolution in a 1 litre Styrofoam box (20 mm wall thickness) plotted in Fig. 13 indicates that the setting time was not affected by the oil or lignosulphonate. Chandra and Xu (1995), on the other hand, claimed substantial retardation if the direct addition of vegetable oil exceeded 0.8 % of cement weight. They reported, however, only strength values for 7 and 28 days.

6.3 Mechanical properties of hardened concrete

Hydrophobizing admixtures do not significantly affect the strength of concrete at 28 days unless a water reducing admixture is included in the formulation. The resulting lowering of the water-cement ratio will then give a higher strength according to Abram's law. Some results for a wax emulsion are given in Table 11 (Brown, 1970) at constant cement content showing giving slight air entrainment, whilst Table 12 gives strengths for a dry brick mix containing a stearic acid based admixture.
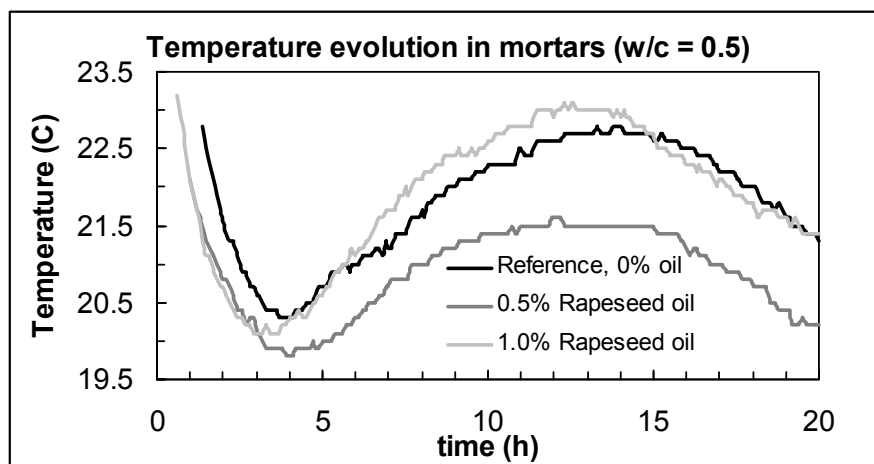
Fig. 13 The temperature evolution of cement paste without and with 0.0, 0.5 and 1.0 % rapeseed oil (Justnes et al., 2004) indicating that setting is not disturbed.

Table 11 Effect of wax emulsion type hydrophobizing agent on the compressive strength of concrete as a function of cement content (Brown, 1970).

Cement content (kg/m^3)	Wax emulsion content (% of cement)	Compressive strength (MPa)
450	0	64.9
	3	62.3
400	0	53.6
	3	54.0
360	0	44.0
	3	42.4
315	0	33.5
	3	33.5
270	0	21.1
	3	22.4
225	0	Too harsh
	3	15.3

Table 12 Effect of stearic acid hydrophobizing agent on the compressive strength of concrete. Mix proportions; cement:sand:crushed limestone = 1:4:6.5, w/c = 0.45.

Hydrophobizing agent (% of cement mass)	Compressive strength (MPa) at	
	7 days	28 days
0	14.2	17.6
1	14.3	18.6
2	15.2	18.2

The compressive and flexural strength of mortar prisms after 1 and 28 days with different types and dosages of oil as studied by Justnes et al. (2004) are listed in Table 13 as mean values with standard deviation for 3 parallels. In addition the total porosity as a sum of all individual porosities obtained from capillary suction of sawn discs in Table 8 is given as comparison. The total porosity is rather constant ranging from 19.2 to 21.1 vol%. The 1 day strength is not

significantly lower than the reference mortars without oil, with the exception of the highest dosage (1.5 % of cement weight) of linseed (22 % reduction), and to a minor extent for the highest dosage of corn and rapeseed (10-12 % reduction). The apparent less retardation (and strength loss) in this case compared to Chandra and Xu (1995) is probably because the oil was dispersed in the water by the aid of lignosulphonate rather than added directly to the mixture.

Table 13 Compressive (σ_c) and flexural (σ_f) strength for mortars with vegetable oil addition measured after 1 and 28 days curing. For the sake of discussion the sum of porosities, $\Sigma\varepsilon_{sawn}$, obtained by capillary suction for sawn specimen in Table 8 are included as well (Justnes et al., 2004).

Oil Type	Dose (%)	$\sigma_{c,1}$ (MPa)	$\sigma_{f,1}$ (MPa)	$\sigma_{c,28}$ (MPa)	$\sigma_{f,28}$ (MPa)	$\Sigma\varepsilon_{sawn}$
None	0 0	22.4±0.4 21.7±1.3	4.8±1.1 4.6±0.1	49.5±0.9 49.7±1.0	7.3±0.3 7.5±0.5	20.0 20.5
Sunflower	0.5 1.0 1.5	20.9±1.3 21.6±1.2 20.0±0.4	4.5±0.1 4.7±0.3 4.6±0.2	47.1±1.2 46.3±1.3 42.4±0.5	6.9±0.3 6.6±0.1 6.4±0.2	19.8 19.7 19.8
Olive	0.5 1.0 1.5	21.0±0.4 20.3±0.3 21.3±0.6	4.2±0.4 4.1±0.3 4.2±0.1	47.1±1.9 43.6±1.3 47.3±1.2	7.1±0.1 7.5±0.6 7.3±0.2	19.2 19.9 20.2
Soya	0.5 1.0 1.5	21.6±0.5 22.9±0.6 20.6±0.8	4.3±0.3 4.4±0.1 4.2±0.1	43.4±1.7 48.4±0.9 41.4±1.1	6.2±0.4 7.0±0.2 5.8±0.5	20.1 19.4 20.3
Peanut	0.5 1.0 1.5	21.7±0.4 21.7±0.7 21.4±0.4	4.5±0.2 4.1±0.3 4.3±0.0	47.1±1.1 42.0±1.1 42.0±1.1	6.7±0.5 6.8±0.5 6.8±0.1	19.7 20.2 19.7
Linseed	0.5 1.0 1.5	20.1±0.2 20.0±0.4 17.2±0.6	4.4±0.2 4.1±0.1 4.0±0.3	42.2±1.5 42.9±1.0 38.7±1.0	6.4±0.6 6.9±0.4 6.5±0.0	21.0 20.4 21.1
Corn	0.5 1.0 1.5	21.4±1.0 20.2±0.8 19.7±0.4	4.5±0.0 3.8±0.2 4.1±0.1	42.1±4.3 41.6±1.4 42.3±0.9	6.2±0.3 6.3±0.4 6.1±0.2	20.9 20.1 19.8
Rapeseed	0.5 1.0 1.5	21.7±0.5 21.9±0.5 19.4±0.4	4.3±0.4 4.5±0.1 4.3±0.1	47.5±1.2 46.2±1.0 41.3±1.5	6.8±0.4 7.0±0.2 6.5±0.2	19.8 19.8 19.5

The 28 day strength is not dramatically lower than the reference (< 15 %), with the exception of the highest dosage of linseed oil (22 % reduction). Flexural strengths were not reduced to any larger degree than the compressive strengths according to Justnes et al. (2004). Thus, the oils or their decomposition products do not seem to obstruct the degree of hydration and are therefore coordinated towards the hydration products CSH and CH rather than the surface of unreacted cement grains.

The compressive strengths for the same mortars with vegetable oils (Justnes et al., 2004) measured after 3 years hydration are given in Fig. 14 (Vikan and Justnes 2006). The 3-year compressive strengths were approximately 30 % lower for samples with oil compared to the reference samples. The 28 day strength of the reference mortar has increased by 100 %, while

samples with oil increased strength by 60-70 % in the same period. Similar strength increase for plain concrete was found by Neville (1977). The strengths do however not show a clear dependency on the oil dosage which indicates that even 0.5 % vegetable oil is sufficient to slow down strength development.
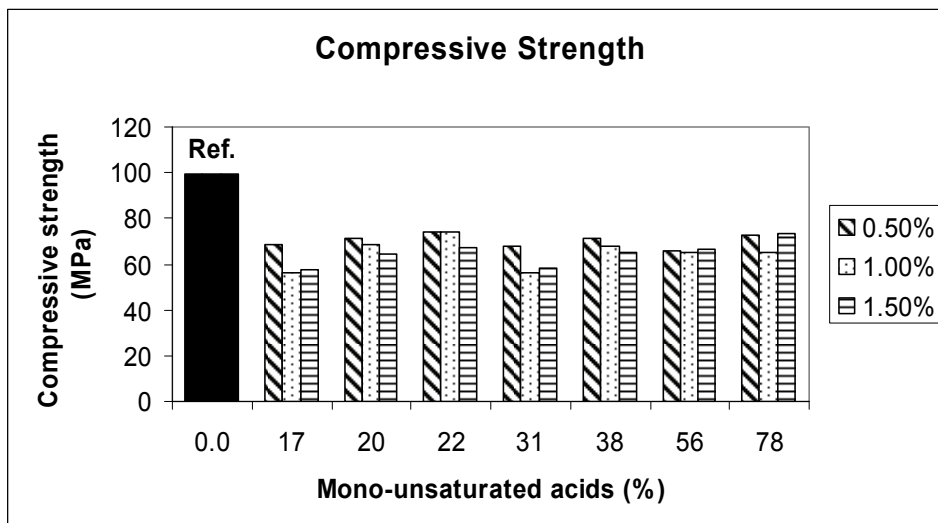

Fig. 14 Compressive strength of mortar samples as a function of oil dose after 3 years moist curing (Vikan and Justnes, 2006)

One reason for lesser strength gain put forward by Vikan and Justnes (2006) was that the transport of water from one part of the microstructure to another may be obstructed when the hydration has proceeded far enough to enrich the oil concentration to become an important phase in the liquid (i.e. oil droplets may block pores). This could also offer an explanation to the lower strength development from 28 days to 3 years versus 1 to 28 days. A second reason discussed for this latter finding might be that the oxygen over time diffuses through the sample and oxidizes the liquid (i.e. mobile) unsaturated fatty acids to a solid saturated fatty acid. Vikan and Justnes (2006) also estimated the degree of hydration of the 3 years old samples and found that this was NOT decreased relative to reference.

In addition to the preceding potential reasons for slower strength gain for mortar with vegetable oil, it is well known that carboxyl acid derivates (occurring in solution when the oils decompose) coordinate strongly with Ca-sites (Ohta et al., 2000). The adsorption of carboxyl acid derivates on the cement particles might alter the hydration both by delaying it and changing the morphology of hydration products. Adsorption of organic additives are known to change the morphology of various materials such as $CaCO_3$, gypsum and hydrated cement (Hekal and Kishar, 1999, van der Leeden and van Roosmalen, 1987, and Shen et al., 2004). Encapsulation of carboxyl acid derivates might therefore have changed the morphology of the hydrated cement phase in a way which has weakened the strength of the paste. The morphology of later products may be more affected than early ones since the concentration of fatty acid increases as the water is consumed.

6.4 Durability of hardened concrete

6.4.1 Aesthetic appearance

It was explained in a previous section that hydrophobizing agents are added to concrete products to reduce the ingress of rain and ground water for aesthetic and hydrophobizing reasons rather to prolong the structural performance of the construction. The improvements in aesthetic qualities

are not short lived, and results (Levitt, 1971) for a stearate based composition over a 10 year period are given in Table 14. The results illustrate the following points:

1. It is necessary to add sufficient hydrophobizing agent so that the absorption at the surface is reduced to a negligible level to obtain best results.
2. The presence of high levels of hydrophobizing agents completely inhibits disfiguring algae growth.
3. The presence of even small amounts of hydrophobizing agents improves the freeze-thaw durability of concrete (Shacklock, 1971).

Table 14 The relationship between the initial surface absorption test and durability of concrete containing various proportions of stearic acid based hydrophobizing agent (Levitt, 1971).

Hydrophobizing agent (% of cement)	Initial surface absorption at 28 days (BS 1881)			Description after 10 years at roof top
	10 min	30 min	1 h	
0.00	0.48	0.28	0.20	Broken by frost, blackened by algae
0.10	0.42	0.25	0.19	Darkened by algae growth
0.25	0.45	0.20	0.17	Slightly darkened by algae growth
0.50	0.43	0.19	0.13	Slightly dirty
1.00	0.33	0.14	0.12	Fairly clean
2.00	0.07	0.04	0.02	Pristine condition

6.4.2 Volume change

Volume changes such as shrinkage and creep are not significantly affected by single drying as shown in Table 15 (Anon, 1970), but shrinkage under drying and wetting cycling (site conditions) will be reduced due to lower moisture uptake.

Table 15 Drying shrinkage of concrete containing varying proportions of a wax emulsion

Wax emulsion (% of cement)	Drying shrinkage of concrete at					
	3 days	7 days	14 days	28 days	56 days	91 days
0	1.05	2.13	2.87	4.68	6.98	8.45
1	0.96	2.10	2.65	4.66	6.82	8.14
2	0.98	2.06	2.47	4.79	6.42	8.00
3	0.75	2.09	2.88	4.61	6.61	7.92

6.4.3 Chloride ingress

In view of the way hydrophobizing agents are working, no improvement in resistance to aggressive gases is expected (e.g. industrial atmospheres). However, the reduced absorption of aqueous media will improve resistance to attack by aggressives, but neutral media, such as sulphates and chlorides. Indeed, the presence of hydrophobizing agents such as high dosages of stearates can completely inhibit the corrosion of reinforcing steel against a fairly high level of chlorides (Gouda, 1970) in the concrete. These hydrophobic admixtures are now being used in the formulation of corrosion inhibitors to get the dual benefit of reducing the ingress of chloride containing water into the concrete and anodic and cathodic protection of the steel (Bobrowski et al., 1992, Krauss and Nmai, 1994, Bobrowski and Youn, 1993, and Berke et al., 1996).

Vikan and Justnes (2006) performed chloride intrusion experiments on mortar with different vegetable oils by storing mortar cylinders of approximately $\phi100 \cdot 200$ mm in a 16 % sodium chloride solution for 6 weeks. The cores of the samples were milled in layers of 1-2 mm and the concentration of chlorides was measured by a spectrophotometric method. The chloride intrusion was quantified by the k-factor:

$$x_{0.1\%} = k \cdot \sqrt{t}$$ [15]

where

$x_{0.1\%}$ [mm] is the depth in the mortar sample where the chloride concentration has reached 0.1 % calculated for one year of exposure to chlorides based on the diffusion coefficient obtained from analysis of the chloride profile by Fick's second law.
k [mm/s] is the intrusion rate (k-factor)
t [s] is the time

Fig. 15 shows an example of chloride intrusion profiles from Vikan and Justnes (2006). The chloride intrusion experiments showed clearly that the oils added to the mortars reduce the amount of chloride which penetrates into the samples. The oils with a high amount of mono-unsaturated oils are stronger chloride "blockers" than the oils with a low amount of mono-unsaturated acids. The chloride intrusion profiles are not altered much by the increase of oil concentration from 0.5 - 1.5 % which indicates that 0.5 % oil addition is enough to "saturate" the pore walls and reduce chloride penetration and binding. The k-factor was found to be reduced by 20 - 48 % by the addition of vegetable oils. The k-factor depended to some extent on the oil concentration as seen in Fig. 16. However, no dependencies between k-factor and concentration of mono-unsaturated acids in the oils were found. Blankenhorn et al. (1978) found similarly that chloride ion penetration into hardened concrete samples impregnated with linseed oil was significantly reduced compared to control specimens.

The chloride intrusion in mortars was greatly reduced by latex additions (Justnes and Øye, 1990, and Justnes et al., 1990 and 1997), but the effect was strongly dependent of the polymer type. Acrylic based latices (Justnes et al., 1992) seemed to be superior.
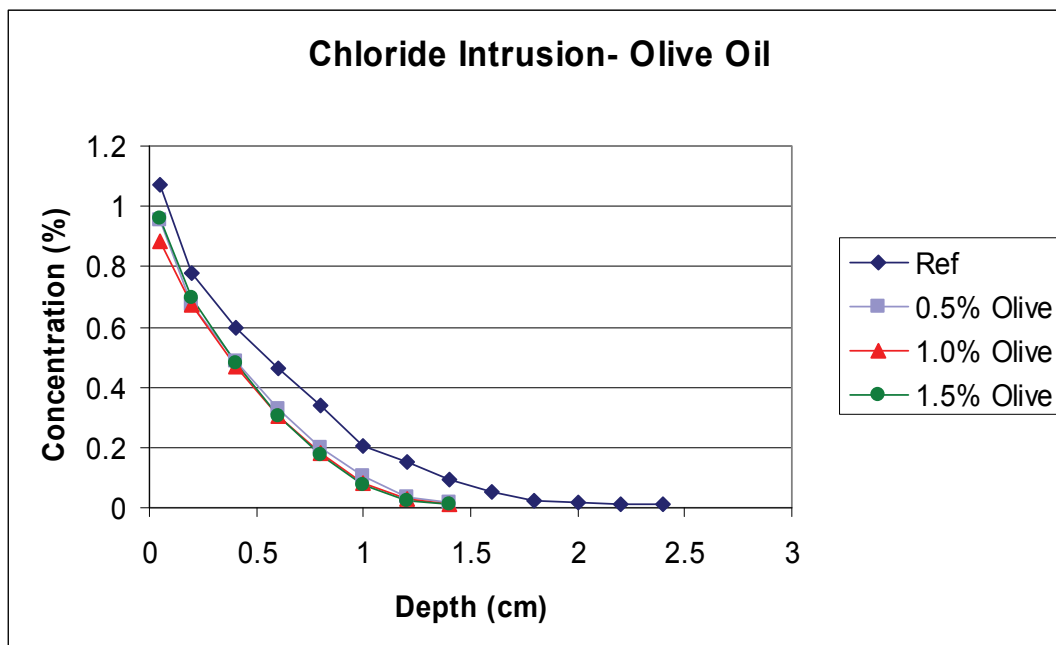
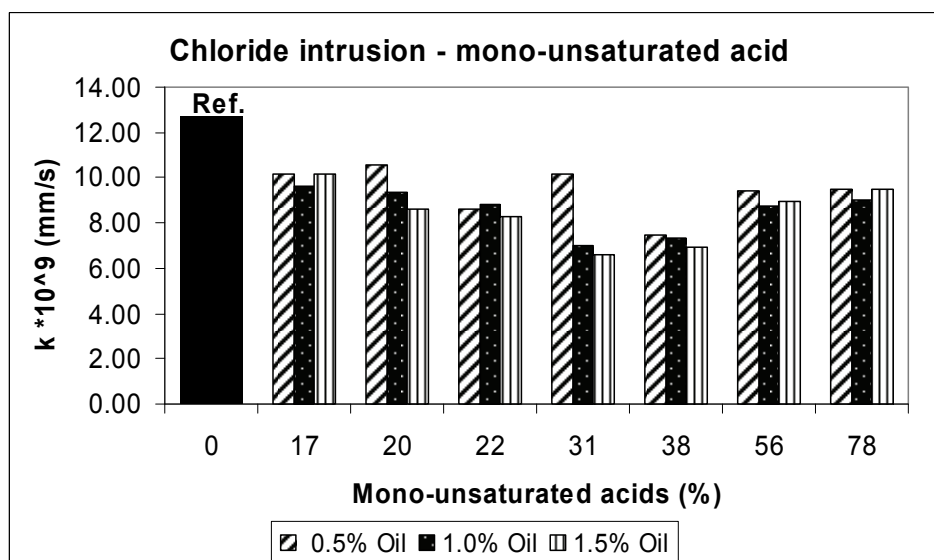Fig. 15 Chloride intrusion profile for mortar samples with 0.5-1.5 % olive oil from Vikan and Justnes (2006)

Fig. 16 Chloride intrusion in mortars measured as the k-factor (mm/s) as a function of mono-unsaturated acids (Vikan and Justnes, 2006).

6.4.4   Carbonation resistance

Vikan and Justnes (2006) studied the carbonation resistance of 3 year old mortars with vegetable oils by storing mortar cylinders of approximately $\phi 100 \cdot 200$ mm in a glove box with 5 % CO_2 for 20 weeks to monitor carbonation. The cylinders where thereafter split and sprayed with phenolphthalein before measuring the depth of carbonation as the grey zone not colored pink by the indicator. The addition of the vegetable oils to the mortars increased the carbonation depth compared to the reference samples as illustrated in Fig. 17. The carbonation depth seems to increase with increasing oil dosage in some instances. There was no clear connection between the

amounts of mono-unsaturated acids in the oils and the carbonation depth. The carbonation depth seemed however to increase with increasing amount of apparent macro pores in the samples as illustrated in Fig. 18. This could mean that the dryer the interior, the faster the carbonation. The share of apparent macro pores in the samples is found to increase with the amount of mono-unsaturated acids in the oils as illustrated in Fig. 9.
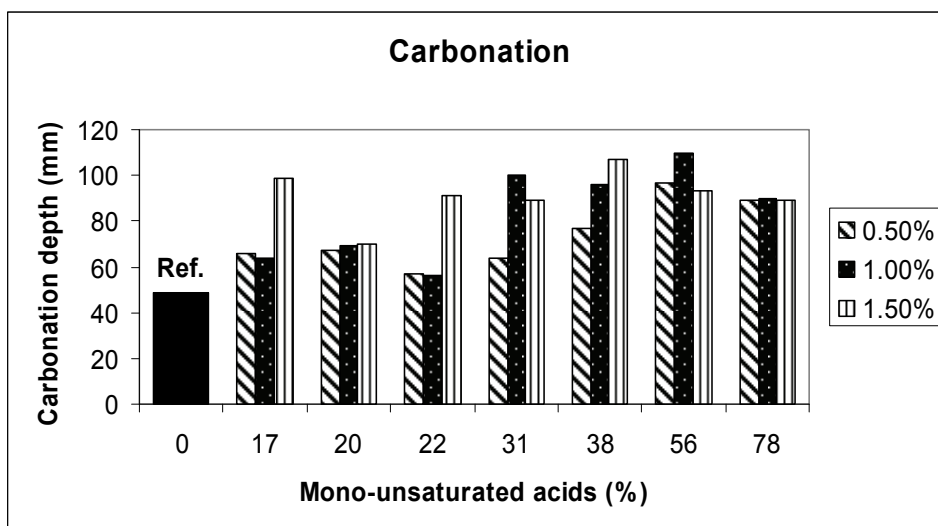

Fig. 17 Carbonation depth (mm) of mortars as a function of oil dosage (%) and content of mono-unsaturated acids in the oils after Vikan and Justnes (2006).
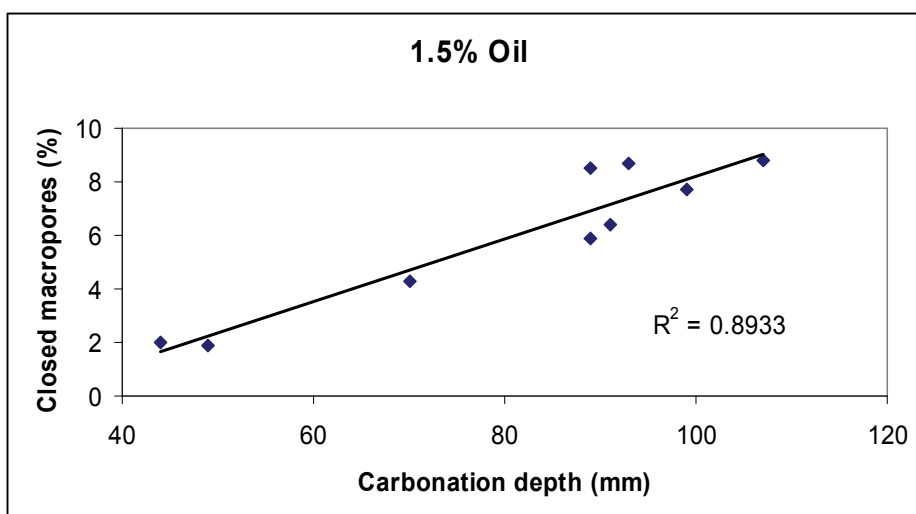

Fig. 19 Carbonation depth as a function of closed macro pores from Vikan and Justnes (2006).

Carbonation resistance of mortars could be increased by latex additions (Øye and Justnes, 1991, and Justnes et al., 1995), but this dependends on polymer type. Some polymers (e.g. polyvinylacetate) even degraded to polyvinylalcohol and consumed hydroxyl ions in the process.

6.4.5   Freeze-thaw resistance

Anon (1970) tested the freeze-thaw resistance of concrete containing wax emulsions and the dynamic elastic modulus versus number of freeze-thaw cycles are shown in Fig. 20. In this case, however, some air-entrainment (4.2 vs. 0.9 vol%) and a reduction in w/c (0.61 vs. 0.70) was obtained that would contribute to the beneficial effect of the wax emulsions.
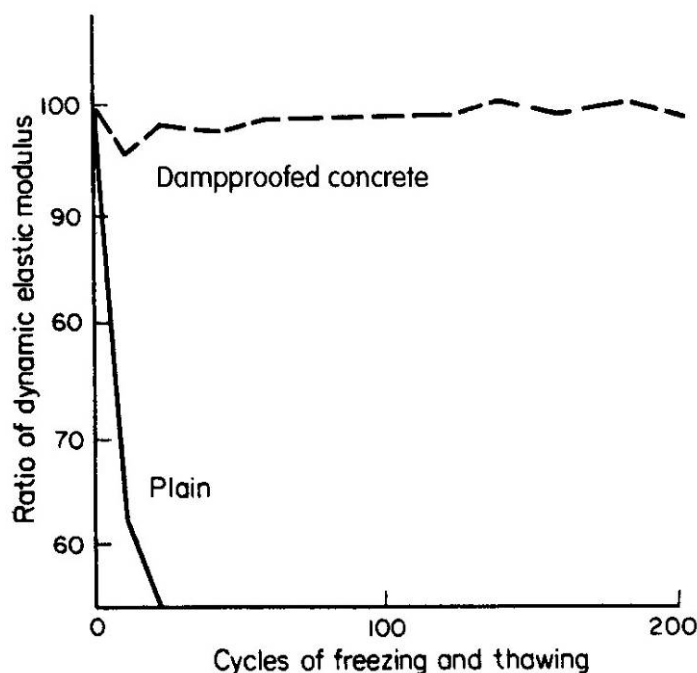
Fig. 20 Freeze-thaw resistance of plain concrete and concrete hydrophobized with wax emulsion. Both concretes had a cement content of 285 kg/m^3 (Anon, 1970).

Justnes (1995) reported freeze-thaw resistance of mortars and concrete modified with latex additions according to the scaling method (Swedish code SS 137236) with salt solution. The conclusion from this study was that the improvement in performance for mortars with latex relative to reference largely was due to the air entrainment of the latex.

7   FURTHER RESEARCH

If investigations on hydrophobizing agents are to be continued, it is recommended to further investigate vegetable oils due to their apparent cost-efficiency and environmental friendliness. According to Gunstone (1996) the ranking of oil production tonnage in the world is from soya > palm > rapeseed > sunflower as the 4 big ones. Palm oil has not been tested, but it has a medium content of monounsaturated (40 %) and unusual high content of saturated fat (44 %), so its performance remains unclear. However, among those tested, rapeseed oil seems to be the best candidate for industrial application in mortar, considering both production volume and performance. In addition, rape can easily be grown in colder climates (like in Norway) unlike palm.

Higher dosages of vegetable oils than 1.5 % may be of interest for other potential effects like hardening retardation, shrinkage reduction, electrical resistivity decrease and pH reduction.

8   CONCLUSIONS

Durability and aesthetic appearance of concrete may be improved by the addition of hydrophobizing agents as a consequence of reduced water absorption.

Hydrophobizing agents lead to less water absorption at the same time as they let water vapour out. This may lead to a dryer interior over time and thereby reduced rate of detrimental reactions needing liquid water as reaction medium. The ingress of water born aggressives like chlorides will be reduced (in particular in marine splash zones), but also corrosion rates may be decreased. Carbonation rates may, however, be somewhat increased.

Vegetable oils seem to be the most cost-effective hydrophobizing agents as good effects may be achieved by a dosage of only 0.5 % of the cement mass. Furthermore, the cheapest and most available vegetable oil based on rapeseed is among the most effective tested.

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