

# EFFICIENCY OF LIQUID MEMBRANE-FORMING COMPOUNDS FOR CURING CONCRETE

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## 1. Introduction

Exposed surfaces of freshly placed concrete have to be coated by a vapour-tight plastic sheet, tarpaulin or a membrane-forming liquid half or one hour after placing, and also other surfaces, shuttered for a while, have to be protected from drying out to at least 7 to 14 days of age. The best methods of curing: water flushing or spraying are restricted to certain cases (e.g. freshly stripped concrete pipe); concretes of runways, pavements and the like are actually treated by mechanically applied membrane-forming liquids. These compounds have to be tested for compliance with official specifications (e.g. [1], [2]) and compared to requirements [3]. Other specifications refer to the control of exemptness of holes of the dry membrane [4].

## 2. Classification tests

Commissioned by the United Chemical Works, manufacturers of such compounds utilized in Hungary, and by Concrete Roads Enterprise, responsible for the construction of motorways and airports, various kinds of oil-in-water, water-in-oil emulsions, synthetics in a solvent etc., Hungarian, Austrian, Swiss, and FRG-made membrane-forming compounds have been compared and classified — in addition to the usual official specifications — by the following methods:

- technology characteristics: *viscosity* by several methods and at different temperatures, *flash point*, *density*, *drying time*;
- features of the ready membrane: *colour* [5], *light reflection* and *friction resistance* by the SRT method (TRRL = Transport and Road Research Laboratory, United Kingdom), as well as *salt absorption* (5% NaCl) to check the protection afforded by residual membrane against melting salt penetration (e.g. during the first winter);
- *bending* and *compressive strength*, *wear resistance*, and *surface (micro) hardness* of concrete (mortar) hardened under the membrane;

- *derivatography* of adsorbed and constitutional water in layers at different depths to determine the hydration degree; and — last but not least —
- *vapour-tightness*, generally determined as *water loss percentage* of control specimens up to 14 days, and sometimes as the absolute water loss up to 72 hours [3],
- in addition to as specified, vapour-tightness has been examined from the aspect of relative efficiency of coatings applied at *equal costs* (Ft/m<sup>2</sup>), as well as the effect of the *coating time* (immediately after placing, when the surface became dull, or delayed) and of the spray rate g/m<sup>2</sup> on the vapour-tightness.

Climatic features in German and Austrian specifications (+30°C and 30% r.h.) correspond to Mid-European climate, as against the ASTM requirements (+40°C and 30% r.h.) but the 72-h requirement of ASTM is superior to average requirements in [2] for 1—3—7—14 days, specifying without rigour a max. water loss by treated 14-day specimens half that by untreated control samples. This latter requirement [2] is met even by compounds failing the ASTM specification.

Let us pick out at random some of the more interesting results of the above tests; otherwise not all characteristics of all compounds have been investigated.

In an attempt to avoid boosting any agent, in the following, manufacturers, country of origin and trade name will be replaced by letters but Table I will indicate the corresponding basic type.

Table I

Membrane-forming compound types and symbols

Group		Symbol
		N (= no agent)
Emulsion	water-in-oil	A, U
	oil-in-water	C
Solvent		D,* E, P, Q, R

\* Subsequently excluded from the tests because of its bituminous black colour

### 3. Checking mechanical characteristics

#### 3.1 Abrasion tests on a Böhme apparatus (table)

Mortar [1] was cast into 7.07 cm cubes; exposed surfaces were coated by agents A, E, P or left untreated (N); after demoulding, free surfaces were smeared by the same agent (x) or in another series by a lubricant (xx) to prevent eva-

poration. Specimens were stored in hoods with dry atmosphere and draught. Two specimens were tested for each type (Table 2). Results permitted to conclude that:

- compared to the control specimen (*N*), all agents are about equally efficient: after-treatment improved abrasion resistance by about 40%;
- uniform abrasion test is not sensitive enough to distinguish between agents, the more so if a small surface compared to the specimen volume is coated (*xx*), justifying the use of slab-like specimens.

**Table 2**  
Abrasion losses (mm)

Symbol	(x) immersed		(xx) grease sealed	
	440 rev.	880 rev.	440 rev.	880 rev.
N = nil	10.0	20.0	—	—
A	5.35	11.75	4.6	9.6
E	6.0	12.65	4.6	10.0
P	6.4	12.8	4.6	9.65
Remark	§	§§	□	□□

Legend: § = at 42 to 46 days, dried at 105°C;  
 §§ = air dry, at 52 to 56 days of age;  
 □ = air dry, at 35 to 36 days of age;  
 □□ = at 50 to 52 days of age, after gradual water saturation.

### 3.2 Bending strength and compressive strength

Mortar [1] was cast into prisms  $4 \times 4 \times 16$  cm and treated as in 3.1. After bending tests, the broken halves were tested in compression, on three specimens for each type (Table 3).

It has been concluded that:

- *bending strength* is a sensitive indicator of coating efficiency, the more so since the retained water adds to bending strength, doubling the effect;
- *compressive strengths* give no indication before drying out;
- the best agents (*P*, *U*) increase the strength by 30 to 70% compared to the control specimen;
- prism specimens do not represent the slab surface/mass ratios of road concretes, neither do they fit coating tests according to [1] and [2] or tests of storage in a curing cabinet.

**Table 3**  
Strength values for  $4 \times 4 \times 16$  cm prisms (kp/cm<sup>2</sup> and %)

Symbol	First series †				Second series §	
	(±)		(x±)		(x)	
	b	c	b	c	b	c †
N = nil	37.3	189	41.5	181	45.0	187 = 100%
P	50.2	321	53.1	250	70.8	262 = 140%
A	43.5	285	47.5	288	61.5	218 = 117%
E	35.5	335	49.9	295	59.9	258 = 138%
U	—	—	—	—	72.0	285 = 153%
D	—	—	—	—	63.2	256 = 137%

§ = 28-day air dry (non-dried)

† = dried at 105°C

b = bending strength

c = compressive strength

### 3.3 Compressive strength of cubes cut out of slabs

Due to the above, further on, slab-like specimens were tested for evaporation losses as specified in [2], then at 14 days they were sawn into 25 mm cubes (leaving them in the plastic pans) and at 24 days, after drying at 105°C, data in Table 4 were obtained. Conclusions drawn from Table 4:

**Table 4**

Vapourtightness efficiency of specimens tested according to [2] and compressive strength of 25 mm sawn cubes

Symbol	Compressive strength kp/sq. cm				Water loss percentage of control specimen [2]				
	Min.	Max.	Avg.	%	24 h	72 h	7 d.	15 d.	avg.
N	197	226	205	100	100	100	100	100	100
P	342	437	384	187	36.4	45.2	53.6	60.0	48.9
A	381	467	421	205	20.4	36.2	43.7	52.7	38.2
Q	468	515	495	241	6.9	25.2	38.1	48.6	29.7
R	483	531	499	244	10.6	23.8	33.4	42.9	27.7
C	485	551	520	254	12.4	39.2	50.6	59.9	40.5
E	461	608	540	263	0.0	0.0	3.9	13.6	4.4

- *compressive strengths* follow in the same *order* as do *water losses* at 72 hours — except for agent *C* (unique oil-in-water emulsion in this series);
  - all agents met *vapour-tightness* specifications [2] (= average loss below 50%); this specification is, however, not strict enough because of the rather different efficiencies of membranes meeting the specification;
  - in spite of its excellent vapour tightness and the high strength of the treated mortar, agent *E* had to be excluded from further tests because of its inadequate viscosity for continuous spraying (Table 5), and of the uneven viscosities at 20°C of consecutive shippings. The manufacturer's suggestion to dilute *E* with petroleum on the site as needed is unacceptable — otherwise contradictory to [3];
  - *consecutive mechanical testing of slabs from vapour tightness tests* has been proven to be convincing for engineers thinking "strength".
- After the described investigation, compounds *A*, *Q*, *R* and *C* have been involved in further tests.

Table 5  
Viscosity-type indices

Symbol	Efflux time, sec.				Viscosity	
	MARCUSSON		DIN cup		cP*	
	+2°C	+20°C	+2°C	+20°C	+2°C	+20°C
tap water	4.8	4.35	11.0	10.5	167	100
<i>R</i>	5.2	5.0	12.0	11.2	80	45
<i>Q</i>	5.2	5.0	12.0	11.4	88	40
<i>C</i>	6.0	5.0	11.4	11.3	Ø	109
<i>P</i>	7.0	5.45	13.9	12.1	184	64
<i>A</i>	28.2	10.3	63.0	23.3	280	64
<i>E</i> §	Ø	10.4	Ø	21.5	Ø	250

\* in a Hoesppler consistometer, cP

§ thixotropic — gelly, non-fluid at low temperature

Ø unmeasurable

#### 4. Spraying time, specific agent consumption, economy

Tests followed [2] except that the mortar used was made with standard sand of three sizes and of a composition similar to the ISO standard mortar for cement testing ( $w/c/a = 0.42/1/3$ ). Lowering  $w/c$  from 0.50 to 0.42 eliminated surface bleeding; setting (seen by dullness) followed 1 h after placing. This  $w/c$  is that for road concretes.

#### 4.1 Effect of spraying time and quantity

Figs 1 and 2 show the respective effects of two different sprayed rates of the cheapest agent *A* (water-in-oil = w/o emulsion); and of white agent *C* sprayed at different times. Rather than as the control specimen percentage, water loss is indicated here as a percentage of the original (mixing) water. Typically, the untreated control specimen (*N*) releases some 50% of its mixing water as soon as at 24 hours, hence the initial w/c = 0.42 is reduced to about 0.21, raising doubts to subsequent hydration.

The two agents are oppositely affected by shifting the *spraying time*: best results are achieved with the w/o emulsion sprayed immediately after placing (suggesting the need of water replacement); o/w emulsion *C* could, however, only de-emulsify and form a membrane on dry support when applied later. (This delay adversely enhances "free" evaporation before spraying the compound.)

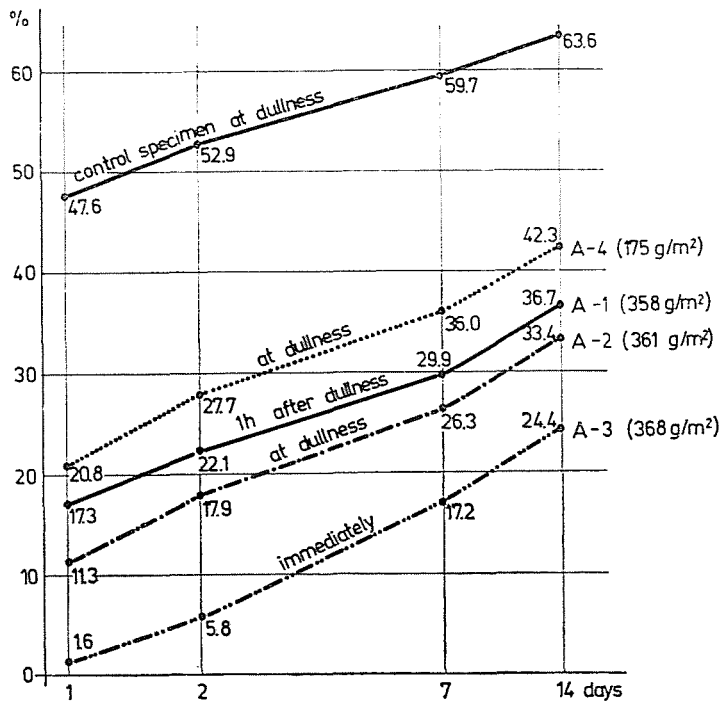


Fig. 1. Effect of spraying times and actual rates of water-in-oil emulsion *A* on vapour tightness in terms of percentage loss of mixing water

## 4.2 Economy

Evaporation losses of slab specimens treated at *identical* (hence other than optimum) times, at about equal costs are seen in Fig. 3. Agent *A* has been applied in the quantity of  $350 \text{ g/m}^2$  in compliance with relevant Hungarian specifications; a greater quantity would run down the slab. Also technologies were uniform (spraying the membrane 1 h after placing) and so were costs save for *A*. Also the relative 50% vapour-tightness requirement [2] curve (specified average) has been plotted. Comparison of agents sprayed at the respective optimum times at about equal costs (save *A*) (Fig. 4) permitted to conclude that:

- applying each agent in the experimentally determined best way yields similar vapour-tightnesses;
- from the aspect of work management it is the simplest to spray just after placing (by a spraying machine following the finisher); it is rather uncertain to wait just an hour *after* dullness;
- synthetics *Q* and *R* in a solvent are superior to emulsions *A* and *C*.

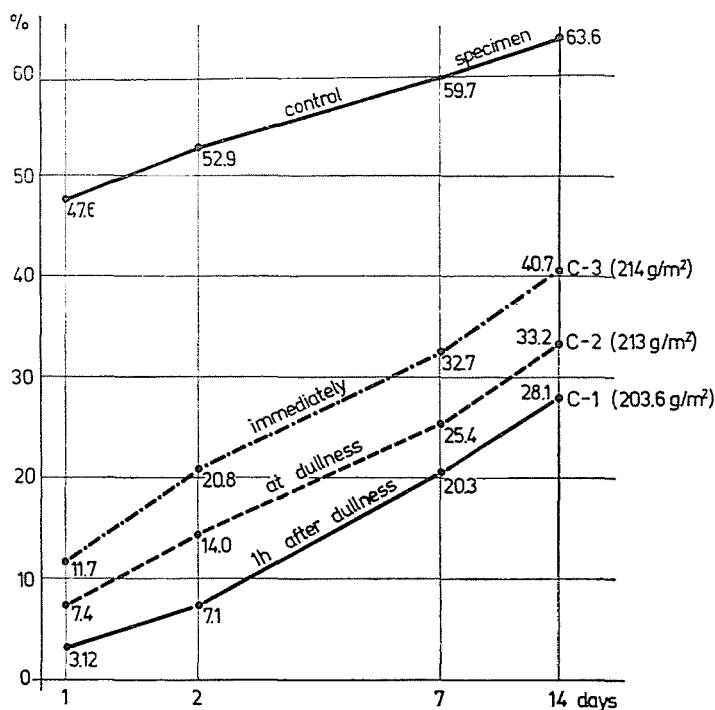


Fig. 2. Effect of spraying times of oil-in-water emulsion on vapour tightness in terms of percentage loss of mixing water

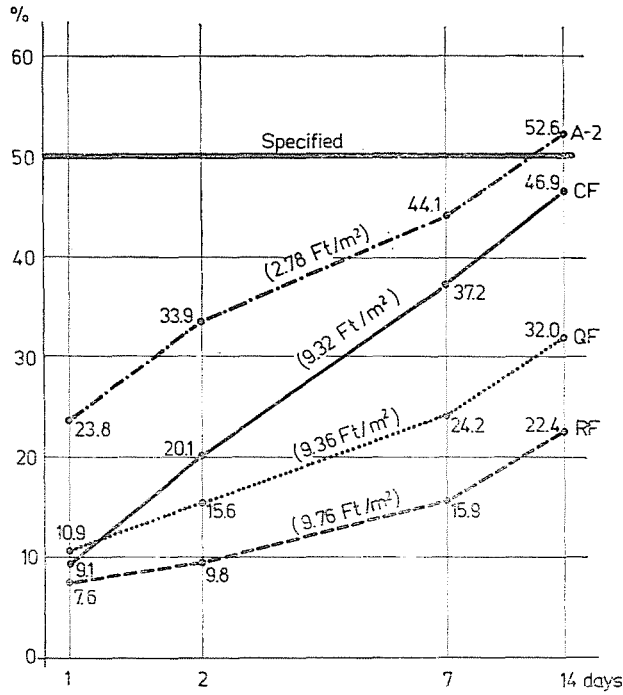


Fig. 3. Water loss under different membrane compounds sprayed at equal times as a percentage of that of the control specimen (cost in Ft/sq. m)

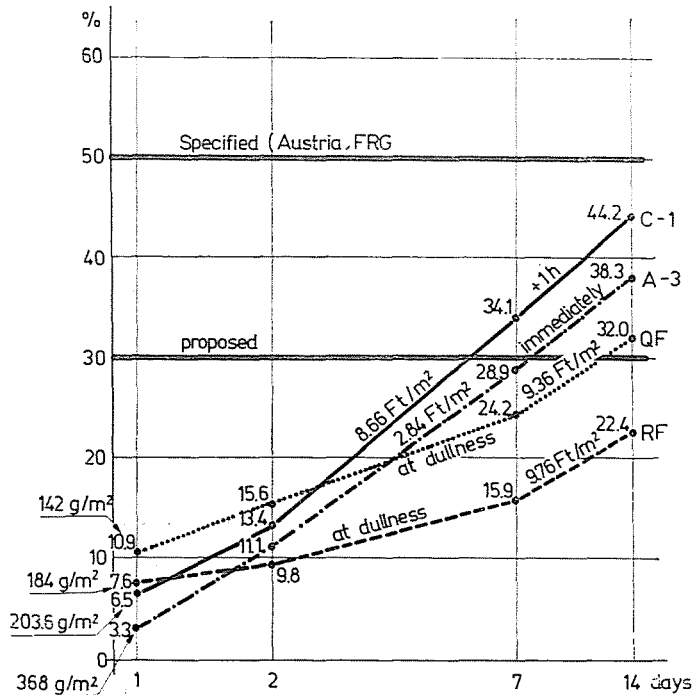


Fig. 4. Water losses under the best membrane types as percentages of the control specimen (N)



Thereafter the relative effect of (rather plentiful) oil in agent *A* on the hardness and hydration of sub-membrane layers compared to other compounds has been investigated.

## 5. Hardness and hydration percentage of layers underlying the vapourtight membrane

### 5.1 Hardness tests

Paste specimens with no aggregate and  $w/c = 0.40$  (!) have been made in slab form and coated with membrane-forming compounds each at the most appropriate time, costs being kept equal (also here, *A* was cheaper).

After a one-week vapour-tightness test, specimens were stripped and immersed in isopropyl alcohol to stop further hydration. After abrading 2 mm each from the top and the bottom of slabs (at the Department of Mineralogy and Geology, Technical University, Budapest) these surfaces have been made checkered to determine top and bottom rebound hardnesses (convertible to Shore hardness values) by dynamic hardness tester for metals "Sclerograph". Meanwhile slabs were soaked in isopropyl alcohol (except test minutes) (I).

Thereafter slabs were air-dried and repeatedly water-saturated and dried to allow ulterior hydration, followed by another hardness test (II) on unused squares of the checkerboard.

Rebound averages from hardness tests I and II are shown in Table 6 for each agent and layer, permitting to conclude:

Table 6

Sclerograph hardness testing of rubbed slabs 23 mm thick (rebound averages and ranges)

Measurement		Symbol	<i>A</i>	<i>C</i>	<i>Q</i>	<i>R</i>
Test I	Top	Mean	6.7	9.1	9.3	9.3
		Range	3.5	3.5	2	3
	Bottom	Mean	10.5	12.5	12.4	11.0
		Range	2.0	3.5	3.0	3.5
Test II	Top	Mean	9.9	13.9	14.2	13.8
		Range	7.0	5.5	4.5	5.0
	Bottom	Mean	13.0	14.8	14.6	14.8
		Range	4.0	2.5	4.0	4.5

Test I: after 1 week in a curing cabinet

Test II: 3 weeks later, after several saturation and air-drying cycles

- this method fits determination of different layer hardnesses and homogeneities;
- according to vapour-tightness tests made also on paste slab specimens, agent *A* was inferior to *C* (as against listed in Fig. 4) impairing, together with the infiltration of w/o emulsion into the top layer, the hardness (strength), not even offset by post-hydration; and
- layers under membranes *C*, *Q* and *R* were harder — this test showed agent *Q* somewhat superior to both others.

## 5.2 Hydration degree

Scratch samples have been taken from the layer under the membrane and from the bottom of the untested halves of slabs in 5.1, and DTA-DTG-TG-T derivatograms recorded.\* (Until test, both specimens and samples were stored in isopropyl alcohol.) Typical water contents are seen in Table 7.

The most of constitutional water belonged to agents *R* and *Q* (column 7 in Table 7). The requirement of constitutional water not to be released but at high temperatures so as to yield much of calcium-silicate hydrates pointed also to the superiority of *R* and *Q* (column 6).

Table 7  
Derivatography data

Water % as a percentage of mixing water							
Symbol	Layer position	Adhesion water $\leq 140^{\circ}\text{C}$	Constitutional water $140-440^{\circ}\text{C}$	Portlandite-bound water $\text{P H}_2\text{O}$	Constitutional water (with that bound to P) $440-1000^{\circ}\text{C}$	Total constitutional water $140-1000^{\circ}\text{C}$	Total water
<i>R</i>	Top	6.52	11.00	5.47	7.71	18.71	25.23
	Bottom	7.64	10.20	5.75	7.60	17.80	25.44
<i>A</i>	Top	4.00!	4.90!	not evaluable			
	Bottom	5.02	9.07	4.91	6.77	15.84	20.86
<i>C</i>	Top	7.82	9.66	5.06	6.98	16.64	24.46
	Bottom	7.66	9.24	5.64	7.65	16.89	24.55
<i>Q</i>	Top	7.41	10.61	5.55	7.30	17.91	25.32
	Bottom	7.74	10.00	5.66	7.72	17.72	25.46
1	2	3	4	5	6	7	8

\* Derivatograms were evaluated by Dr. Margit Boros, chemical eng.

From the aspect of water bound to portlandite, hence of the proportion of water in crystalline  $\text{Ca}(\text{OH})_2$ , first comes  $Q$  and then  $R$  (column 5).

Adherent water, of importance in the ulterior hydration process, permits an initially insufficiently hydrated cement to achieve or at least to approach an adequate hydration degree, as seen in column 3, indicating the order of agents  $C$ ,  $Q$  and  $R$ . Oil infiltration in the top layer with agent  $A$  made evaluation meaningless. (Also  $C$  behaved initially poorer.)

Results show agents  $R$  and  $Q$  to be the best, in agreement with other test results (columns 7 and 8 in Table 7).

## 6. Salt absorption

To examine how much the formed vapourtight membrane transmits the melting salt in winter to the concrete, another test series was made with the same agents as before, also on slab-shaped specimens. One week after application, half of the specimens were brushed, the other half rubbed and then the edges sealed.

Thereafter they had been immersed in 5% sodium chloride solution until 24 days of age.

Membrane forming compounds were applied in quantities according to economy aspects in item 4 to yield data compiled in Table 8. After brushing down to simulate the effect of vehicle traffic, results show agents  $R$  and  $Q$  to be the best sealants, hence of the lowest salt transmittance.

Rubbing down was no adequate test method, likely to be unrealistic by membrane rests obturating and thus sealing pores.

A concrete layer underlaying a good membrane was seen in this testing arrangement not to absorb more than 3.0 to 3.5% of salt solution.

Table 8  
5% sodium chloride absorption

Symbol	Applica- tion rate g/sq · m	Absorbed percentage by weight			
		brushed slab		rubbed slab	
		10 days	24 days	10 days	24 days
$R$	167	2.85	3.05	1.76	2.21
$Q$	126	2.92	3.16	1.83	2.24
$A$	327	3.90	4.20	1.36*	1.82*
$C$	203	4.70	5.06	1.93	2.29

\* Upon rubbing, the applied water in-oil-emulsion obturates pores

## 7. Checking membranes for porosity

50 sq. cm areas were marked on surfaces of specimens stored in curing cabinets. 10% HCl solution, 1% phenolphthaleic solution in alcohol and in water, resp., have been poured on it, applying the VSN specifications to the sense [4]. Under the effect of hydrochloric acid, membrane *A* sparkled throughout its surface (by degaging CO<sub>2</sub> from lime carbonate), under phenolphthalein it became all violet; all these show the high porosity of the membrane.

Under the same treatment, 8 to 10 spots of membrane *C* sparkled and 20 to 25 spots became violet. (Both are emulsion membranes.)

Hydrochloric acid indicated no fault in solvent membranes *Q* and *R* — a few were indicated by phenolphthalein.

Thus, *membrane types* are rather *different* by transmittance, also shown by vapour losses.

The test by aqueous solution of phenolphthalein seems to be adequate for laboratory and site testing of membranes.

## Summary

Hungarian and foreign-made solvent and emulsion membrane-forming compounds (liquids) have been compared for characteristics beyond those in ASTM and German specifications. Tests covered water loss of specimens during storage in the standard curing cabinet, as well as compressive and bending strength, abrasion resistance under a vapourtight membrane, micro-hardness and hydration degree (by derivatograms) of layers at different depths under the surface, and salt absorption — in addition to usual technology characteristics of the agents (viscosity, drying etc.). Also porosity (point holes) of the ready membranes has been checked. Keeping costs identical, liquid membrane-forming compounds in a solvent *Q* and *R* were the best, followed by an oil-in-water-type white emulsion *C* and a water-in-oil emulsion, cheaper than the others but inhibiting top layer hydration and giving a slow drying, porous membrane. Also efficiency as a function of the spraying time has been determined.

## References

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