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Hygroscopicity of Linear Alkylbenzene Sulfonates Powders

Part 1

Humidity tests have been carried out to study the hygroscopicity of Linear Alkylbenzene Sulfonates (LAS) powders. Several parameters have been considered in this investigation such as:

- The starting LAB (Linear Alkylbenzene) type: molecular weight, composition and homologue distribution
- The HLAS (Alkylbenzene Sulfonic Acid) composition: free-oil amount and composition
- The inorganic counter ion: Sodium, Magnesium and Potassium
- Water addition

The experimental results herein described show that among the parameters studied, the inorganic ion has the strongest influence on hygroscopicity behaviour of LAS powders. Another important finding of this research is the surprising effect of water addition.

Die Hygroskopizität linearer Alkylbenzolsulfonat-Pulver. Feuchtigkeitstests wurden durchgeführt, um die Hygroskopizität linearer Alkylbenzolsulfonat (LAS)-Pulver zu untersuchen. Verschiedene Parameter wurden dabei in die Untersuchungen mit einbezogen, wie z. B.:

- Der Anfangstyp an LAB (Lineares Alkylbenzol): Molekular Gewicht, Zusammensetzung und Homologenverteilung
- Die HLAS (Alkylbenzolsulfonsäure) Zusammensetzung: Anteil an freier Säure und Zusammensetzung
- Das anorganische Gegenion: Natrium, Magnesium und Kalium
- Die Wasser-Addition

Die hier beschriebenen experimentellen Ergebnisse zeigen, dass unter den untersuchten Parametern das anorganische Gegenion den stärksten Einfluss auf das hygroskopische Verhalten von LAS-Pulvern besitzt. Ein anderer wichtiger Aspekt dieser Forschung ist der überraschende Effekt der Wasser-Addition.

1 Introduction

Granules containing high levels of Na LAS are very hygroscopic, and take up moisture rapidly at higher relative humidities resulting in soft sticky granules that are impossible to handle. To solve or to minimise this susceptibility of surfactant powder to caking, a work plan was established and different routes proposed such as:

- To study the effect of starting LAB
- To study the effect of free-oil content and composition
- To use alternative counterions
- To use co-actives and/or builders

The present investigation has led to new findings that have made progress in fundamental understanding of LAS hygroscopicity. The results are herein depicted.

2 Experimental

LAS Granules Manufacture: A laboratory technique developed by Unilever Research has been used. In principle a given amount of HLAS (sulfonic acid) was added to a given amount of one of different inorganic salts such as Sodium, potassium and magnesium carbonate in a Moulinette mixer. The neutralisation end point was detected just before the powder became soft. According to this method the following average results were obtained:

Inorganic salt	Sodium carbonate	Magnesium carbonate	Potassium carbonate
Active matter*	30 %	36 %	22 %

* Expressed as HLAS sulfonic acid (weight %)

Measurement of Powder Hygroscopicity: Unilever Research method.
Enclosed environments can be set up to give a range of different relative humidities, using one of a number of inorganic salts. The humidities are produced within a closed space, when an excess of the solid salt is in contact with a saturated aqueous solution of said salt.

Each humidity environment is set up by placing approximately 500 g of the required salt in a large crystallising dish and adding sufficient deionised water to just cover the salt. The dishes set up in this way are then placed in a 10 litre plastic container, covered with a wire mesh and the container sealed with a tightly fitting lid.

Approximately 2–3 grams of each sample to be tested is added to a pre-weighed crystallising dish and the accurate total weight noted. One sample should be prepared for each humidity set-up. One of each sample to be evaluated is then placed into each container and the lid tightly sealed. The containers are then left at room temperature for two weeks. The water uptake of each sample is determined by calculating the weigh difference after storage. The measured relative humidity for each inorganic salt is shown in Table 1.

Assessment
Each sample was assessed for its flow characteristics and graded on a 1 to 7 scale, where the flowing ability of the powder diminishes as the number increases. The assess-

Saturated salt	Lithium Chloride	Calcium Chloride	Potassium Carbonate	Magnesium Nitrate	Sodium Chloride	Sodium Sulphate
Relative humidity %	12	32	45	54	77	93

Table 1 Relative Humidities (RH)

ment is made after removing each sample from the closed box, by gently tapping the side of the dish, and visually evaluating the extent of caking in the dish, according to the following scale:

Scale	1	2	3	4	5	6	7
Visual Assessment	Free flowing				Caked	Sticky	Very sticky

3 Results and Discussion

3.1 Influence of LAB type

This experiment was conducted with five different commercial LAB's (Linear Alkylbenzenes). The distributions and compositions of the starting LAB's are reflected in Table 2 while the compositions of the HLAS (Linear Alkylbenzene Sulfonic Acids) are depicted in Table 3.

AlCl3 (1): Starting material, chloroparaffins. AlCl3 (2): Starting material, olefins.

- The influence of 2-phenyl content was studied by comparing LAB2 versus both LAB3 and LAB5.
- The influence of molecular weight has been studied by comparing LAB1 vs LAB2.
- The influence of impurities like tetralins is studied in LAB4.

The results are given in Figs. 1 and 2.

Very good behaviour is observed in all the samples up to 54% RH (Relative Humidity) while no significant differences appear between any of the LAS-Na samples tested.

	LAB1	LAB2	LAB3	LAB4	LAB5
Process	HF	HF	Detal	AlCl3 (1)	AlCl3 (2)
< Ph-C10	1.3	1.0	0.3	–	–
Ph-C10	17.2	10.8	10.0	15.3	11.7
Ph-C11	54.6	36.4	35.4	31.6	32.4
Ph-C12	25.3	30.6	28.6	28.9	31.8
Ph-C13	1.6	20.1	23.6	23.1	23.8
Ph-C14	–	1.1	2.1	1.1	0.3
2-Phenyl	16.9	15.5	28.2	29.2	29.6
Tetralins	0	0	0	8,5	0
M.W.	233.3	240.2	241.6	240.4	241.3

Table 2 LAB's compositions and distributions

HLAS	HLAS1	HLAS2	HLAS3	HLAS4	HLAS5
% A.M.	97.1	97.4	97.3	96.6	96.4
% Free-oil	1.5	1.3	1.3	1.5	1.7

Table 3 HLAS compositions

3.2 Influence of free-oil content and composition

- Free-oil content

A substantial amount of free-oil was extracted with hexane from an HLAS2 sample, then, different aliquots of the latter were doped with free oil (from 0,5 % up to 3 %) to obtain the samples to be tested. As can be observed in Fig. 3 and 4 no difference appears between the samples tested.

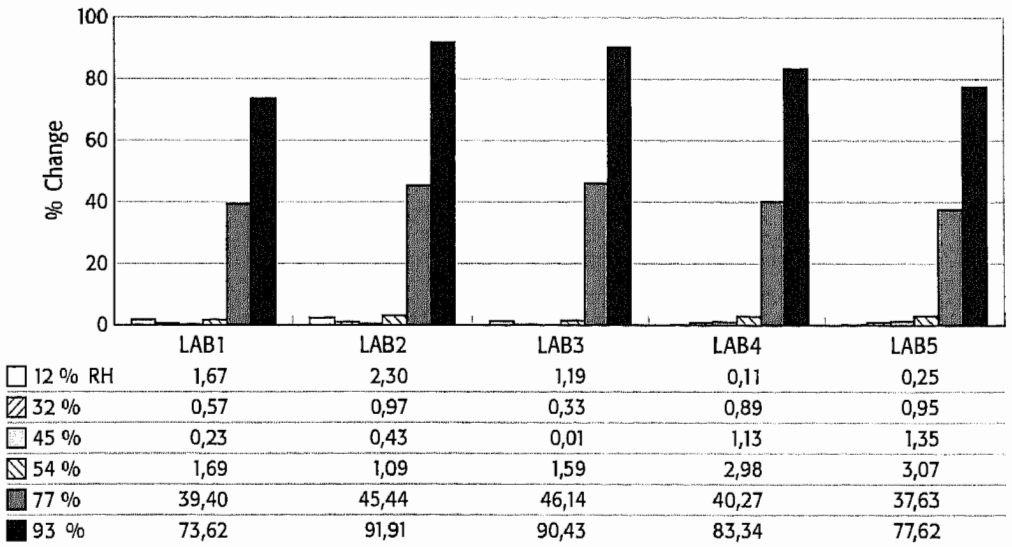


Figure 1 Water uptake: Weight % change after 15 days storage. LAS Na salt. 35 g of each HLAS sample were neutralized with approximately 75 g of sodium carbonate

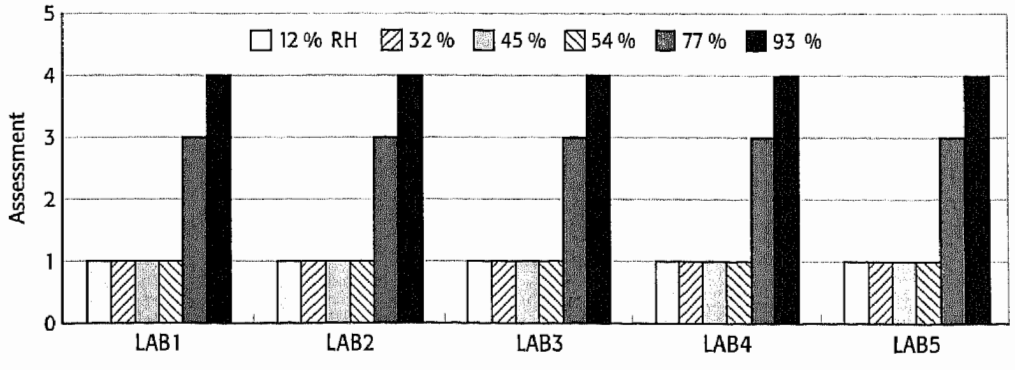


Figure 2 Assessment. LAS Na salt. 35 g of each HLAS sample were neutralized with approximately 75 g of sodium carbonate

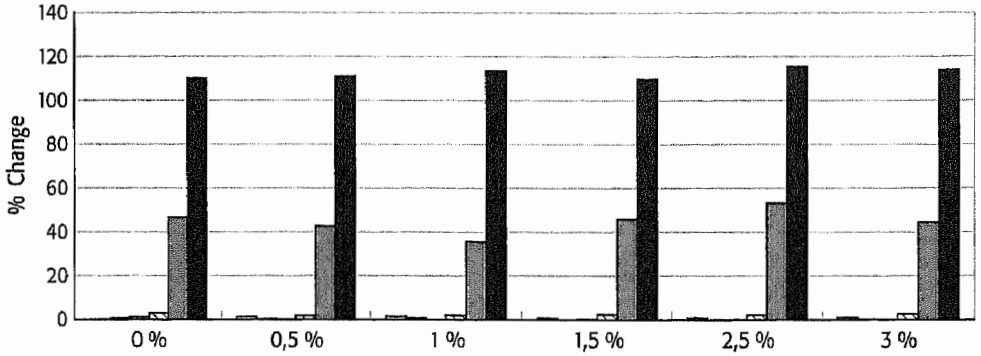
Free-oil composition

Free-oil is mainly composed by non reacted LAB and Sulphones. As it is well known (1, 2), a sulphone consists of two LAB homologues separated by an SO_2 group.

Different samples were prepared with various LAB and sulphone contents up to 4 %. The results obtained confirm that neither free-oil amount nor composition have signi cant influence on RH behaviour.

3.3 Influence of counterion

This experiment has been conducted by using different inc ganic counterions. The sample neutralised was HLAS2.



	0 %	0,5 %	1 %	1,5 %	2,5 %	3 %
12 % RH	0,06	1,45	1,52	0,84	1,02	1,06
32 %	0,80	0,50	0,74	0,06	0,20	0,40
45 %	1,21	0,18	0,06	0,38	0,24	0,14
54 %	2,91	1,86	2,12	2,45	2,17	2,66
77 %	46,81	42,77	35,64	45,90	53,35	44,60
93 %	110,10	111,18	113,60	109,83	115,54	113,93

Figure 3 Water uptake: Weig % change after 15 days storag LAS Na salt. 35 g of each HLA sample were neutralized with approximately 105 g of sodiun carbonate

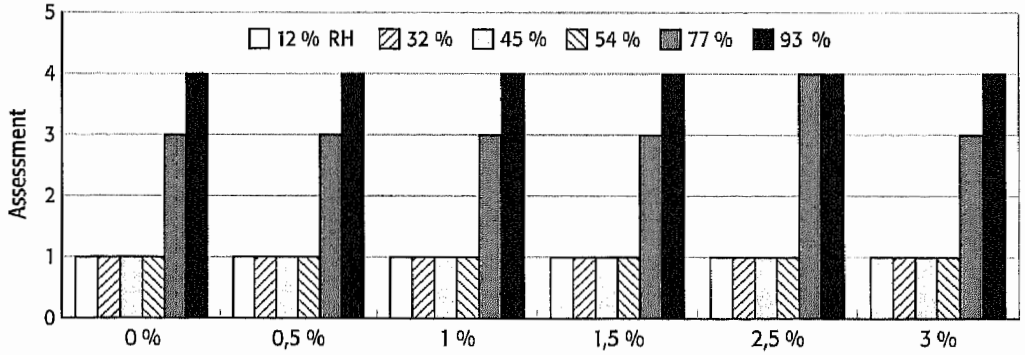
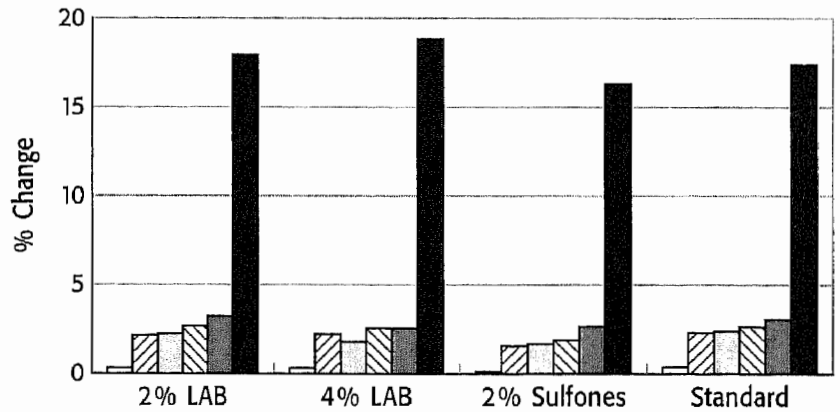


Figure 4 Assessment. LAS N salt. 35 g of each HLAS sampl were neutralized with approximately 105 g of sodium carbo nate



	2% LAB	4% LAB	2% Sulfones	Standard
12 % RH	0,32	0,32	0,12	0,40
32 %	2,15	2,21	1,55	2,31
45 %	2,23	1,79	1,67	2,39
54 %	2,67	2,55	1,88	2,66
77 %	3,23	2,71	2,67	3,06
93 %	17,94	18,84	16,32	17,40

Figure 5 % Change. A standard HLAS sample was doped with different amounts of LAB and Sulfones and neutralized

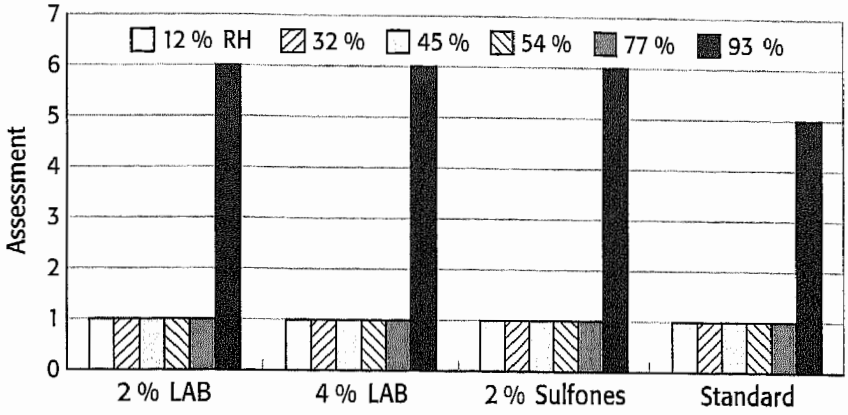
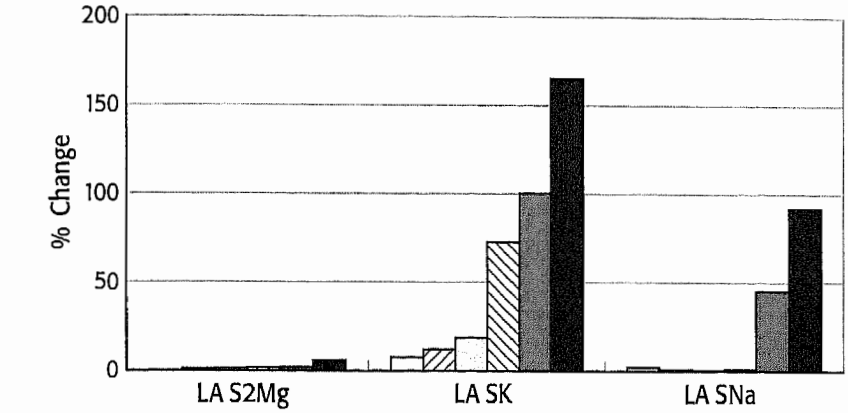


Figure 6 Assessment. A standard HLAS sample was doped with different amounts of LAB and Sulfones and then neutralized



	LA S2Mg	LA SK	LA SNa
12 % RH	0,16	7,71	2,30
32 %	1,18	12,15	0,97
45 %	1,40	18,80	0,43
54 %	1,65	72,74	1,09
77 %	2,03	100,54	45,44
93 %	5,87	165,32	91,91

Figure 7 Water uptake: Weight % change after 15 days storage

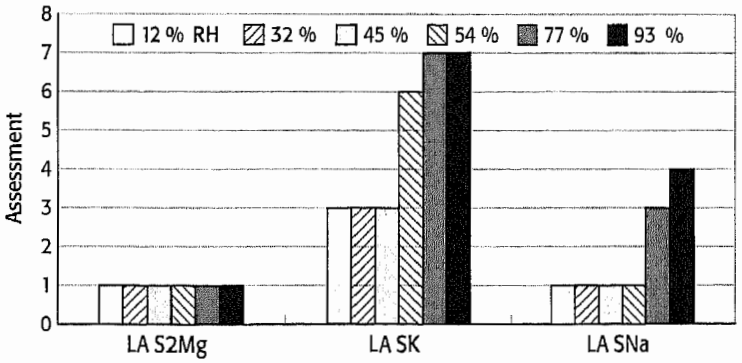


Figure 8 Assessment. Mg, K and Na sulfonates

LAS_2 Mg was obtained by mixing 36 g of HLAS with 64 g of $MgCO_3$.

LAS K was obtained by mixing 35 g of HLAS with 120 g of K_2CO_3.

LAS Na was obtained by mixing 35 g of HLAS with 75 g of Na_2CO_3.

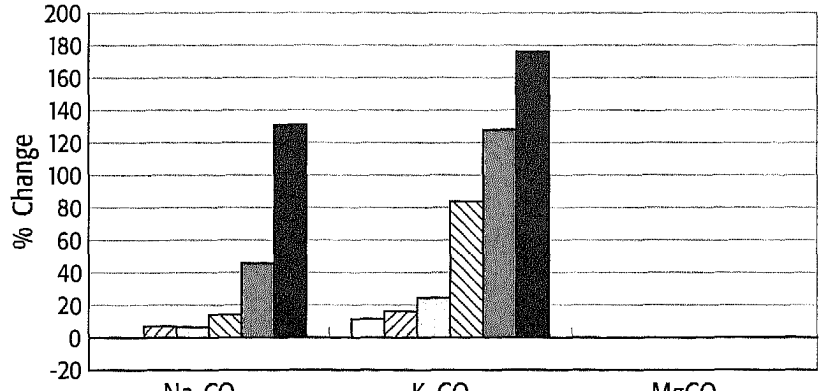
The results plotted in Fig. 7 and 8 show for the first time an excellent performance for LAS_2 Mg salt and a very bad one for LASK.

Considering the preparation method used, LAS granules need the contribution of two components: HLAS itself and the carbonate. Therefore, the study of LAS hygroscopicity cannot be viewed without taking into account the determining influence of the inorganic salt used for the preparation of granules, since the active ingredients are within 22 to 36 % interval, therefore, the remaining product is the salt. This implies that both the counter ion and the inorganic salt may have strong influences on hygroscopicity. This point was checked so as to determine the amount of water uptake by each inorganic salt used in the study.

In this experiment the water uptake of all the inorganic salts used in the study was determined. The results plotted in Figure 9 show as expected, $MgCO_3$ to be the least hygroscopic while Na_2CO_3 and K_2CO_3 are significantly more hygroscopic salts.

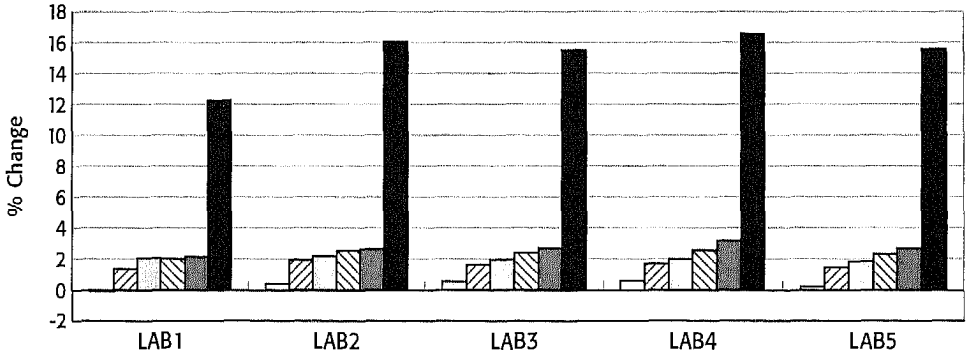
3.4 Study of Magnesium sulfonates LAS_2Mg

3.4.1 Concerning water uptake, no significant differences appear between the different magnesium sulfonates samples. Regarding assessment, performances are almost the same, very good ones up to 77 % RH. Two conclusions can be drawn from the results shown in Figures 10 and 11:



	Na_2CO_3	K_2CO_3	$MgCO_3$
12 % RH	0,10	11,50	-0,35
32 %	7,00	16,00	-0,25
45 %	6,40	24,30	-0,30
54 %	14,00	83,80	0,10
77 %	45,70	128,00	0,25
93 %	131,00	176,20	0,50

Figure 9 Water uptake: Weight % change after 15 days storage. Carbonates salts



	LAB1	LAB2	LAB3	LAB4	LAB5
12 % RH	-0,10	0,42	0,56	0,62	0,24
32 %	1,36	1,94	1,63	1,70	1,46
45 %	2,06	2,20	1,98	2,03	1,86
54 %	2,02	2,54	2,40	2,58	2,32
77 %	2,16	2,66	2,72	3,21	2,72
93 %	12,28	16,08	15,53	16,60	15,61

Figure 10 Water uptake: Weight % change after 15 days storage. LAS_2 Mg salt. 35 g of each HLAS sample were neutralized with approximately 48 of magnesium carbonate (A.M. 43 %)

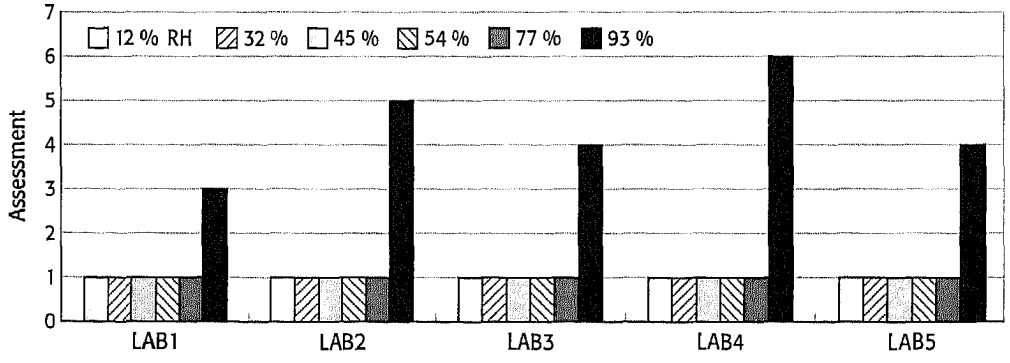


Figure 11 Assessment. LAS_2 Mg salt. 35 g of each HLAS sample were neutralized with approximately 48 g of magnesium carbonate (A.M. 43 %)

- LAS_2 Mg salts show a very low hygroscopicity whatever the HLAS type used.
- Once again it is confirmed that, neither LAB molecular weight, nor LAB composition seem to have influence on LAS hygroscopicity.

3.4.2 Effect of water addition

Water was added to several samples of HLAS2 in different amounts, ranging from 2 to 6 weight %. Each sample was then neutralised with $MgCO_3$ according to the Moulinette method.

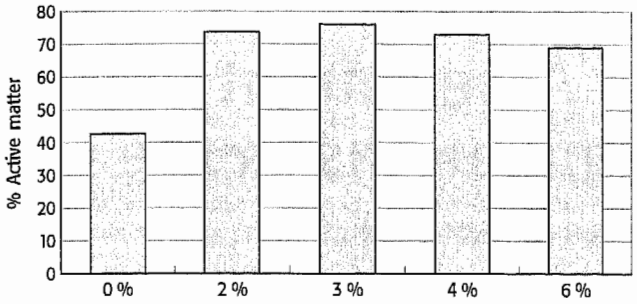


Figure 12 LAS_2Mg salt. Active matter vs water added

The results plotted in Figure 12 show a dramatic increase of active matter when water is added from 42 % with no water addition up to 76 % at 3 % water added.

The role of water is somewhat surprising. It may be acting as a structurant by speeding up the neutralisation of the LAS acid and magnesium carbonate. Improvement obtained by adding water, seems to indicate that because of the very low $MgCO_3$ hygroscopicity, water helps, allowing more HLAS to be dispersed and neutralised.

4 Conclusion

Three important conclusions can be drawn from the results obtained in the first part of this research:

- The hydrophobic part of the anionic molecule has no effect on the hygroscopicity of LAS granules.
- Mg counter ion is the best suited for minimising caking in the manufacture of LAS powders.
- Water addition significantly improves the rate of neutralisation.

In a further communication, other experimental results, such as the optimisation of neutralisation method, the addition of co-surfactants and builders and the study of other parameters will be presented.

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2. *Cohen, L.*: Effect of the molar SO_3/LAB ratio on free-oil amount during LAB Sulphonation, Tenside Surf. Det. *34* (1997) 332.

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