

STUDIES ON RUBBER BASE IMPRESSION MATERIALS

[PART IX] METHODS OF RETARDING THE CURE RATE OF THE POLYSULFIDE IMPRESSION MATERIALS

BY

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INTRODUCTION

It had been very eagerly asserted by the author¹⁾ to take as much as possible the cautions on the surrounding temperature, before discussing about the "accelerators" or "retarders".

We should bear in mind very firmly on that in case of continuing the research about just the reverse direction of the preceding case of "accelerators", namely about "retarders".

It was reported that fatty acids and several metallic fatty acid salts function as cure "retarders" for the lead dioxide cure, and on the addition of "retarders", the set and the cure times were usually extended to about 8 times and 5 times in each, according to the Thiokol Chemical Corporation²⁾.

The report said materials that were commonly used as "retarders" were stearic acid, oleic acid, lead stearate and aluminium distearate; and in case of the oleic acid, a liquid at room temperature compared to the solid stearic acid and others, was employed in compounds requiring good fluidity, but it was not so effective as stearic acid and incompatible with polysulfide beyond 3 parts.

It also said lead stearate and aluminium distearate were required slightly greater amounts as compared to stearic acid to subject the duty as "retarders".

Referring to the above mentioned report for the case of the ordinary polysulfide cure, the author wishes to try their application on the case of our impression materials.

In the ordinary case of the polysulfide cure, the "retarders" are used to extend the cure time in order to result a good quality of the product, otherwise in our case of impression materials, it would not occur to use with such a sense.

What we need about our case of impression materials is the retarding method that would be taken part in the high surrounding temperature compared to that would be expected when those impression materials were made.

The another case of the utilization of these retarding methods would be caused when we need some more times to treat with any special case in clinics or some other places.

In order to prepare for any happenings to be treated with, it is still neces-

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sary to research on such retarding methods to grasp the most effective way as possible as we could do.

EXPERIMENT I

On the retarding method due to the stearic acid

Method of experiment:

a) Prepare both A and B-agents as following compositions;
 A-agent; polysulfide liquid polymers (about 4,000 in molecular weight) .74.6%,
 ZnO .5%, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$.5%, sulfur (S) .0.4%
 B-agent; PbO_2 .14%, MnO_2 .42%, ZnS .18%, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$.5%, Castor oil .21%

b) Prepare each quantity of the stearic acid powder, and mix it into the B-agent that is taken on a piece of thick paper in order to be prepared itself for the mixing operation with the A-agent that is also prepared on the another piece of thick paper. Each quantity of A and B-agents to be taken is 50g either, and the stearic acid employed are 0g, 1g, 3g, 5g and 10g in each.

c) Mix together intensively both A and B-agents by means of a hand spatula reciprocating to and fro, pressing down the substance upon the paper during 50 seconds.

d) Put the mixed substance of A and B-agent into a crucible, and insert a mercury thermometer into that substance. This operation must be completed

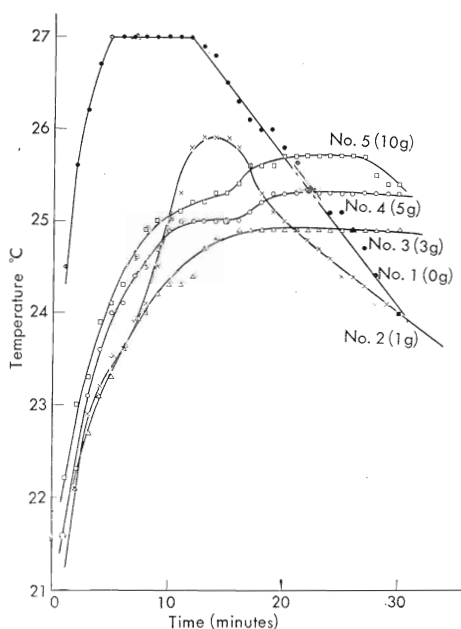


Fig. 31. Retarding method due to stearic acid

within 10 seconds.






e) Begin the recording of temperature with the thermometer just when one minute has passed after the above mentioned preparations had been completed.


f) When the setting of polysulfide is completely finished, take off the polysulfide impression from the crucible and record the various properties of the product.

Results of experiment: Fig. 31 illustrates the temperature-time diagrams corresponding to the various quantities of the stearic acid, being mixed during the mixing operation of A and B-agents, and Table 14 shows the results of various measurements about their products.


Referring to the above described Fig. 31 and Table 14, following items have been understood.

Table 14. Properties of the products, when stearic acid is employed as a retarder
Conditions of experiments; Room temp. . . 19°C, Relative humidity . . . 60%,
Time used in mixing operation . . . 50 seconds

Properties No. of Experiment	Hardness (Shore)	Elasticity (Shore)	Impression Surface	Form of Temp.-time diagram	Stearic acid added per 100g
1	60	95	Fair		0g
2	45	90	Fair		1g
3	30	85	Fair		3g
4	20	80	Good		5g
5	25	85	Good		10g

a) In case of experiment No. 1, when no stearic acid was mixed, the temperature-time diagram became the typical *trapezoid type*³⁾ ().

b) In case of experiment No. 2, when 1g of stearic acid per 100g total quantity of A and B-agents was mixed, the diagram became very questionable form, that appeared very complicate and was thought as if some forms were mixed up together. The product of this case showed lower in both hardness and elasticity than that of No. 1. The diagram told us clearly the effective retarding action of the stearic acid.

c) In case of experiment No. 3, when 3g stearic acid per 100g total quantity of A and B-agents was mixed, the diagram transformed to the very typical *saturant type*³⁾ () , being influenced with intensive retarding action due to the increase in quantity of the stearic acid. This case of transformation resulted the more dropping of hardness and elasticity compared to the previous case.

d) In case of experiment No. 4, when 5g of stearic acid per 100g total of A and B-agents was mixed, the diagram illustrated the two stages of saturant curve that would perhaps be caused by the unfavorable dispersion of the

stearic acid into the mother substance. The product of this case was so much influenced as it seemed to exceed the critical point that would be able to employ for our purpose.

e) In case of experiment No. 5, when 10g of stearic acid per 100g total of A and B-agents was mixed, the diagram showed almost the like as the previous case, and about the product, too, it showed almost the like.

f) Considering from the above mentioned items, it would be concluded that the influence of retarding action due to the stearic acid is recognized sufficient even with 1g per 100g total of the mother substance, and we should be care not to use the quantities of the more to prevent the drop down of the quality.

EXPERIMENT II

On the retarding method due to the oleic acid

Method of experiment:

a) Prepare the A and B-agents of the same compositions as in the case of Experiment I.

b) Take 25g each of both A and B-agents and mix them together just as we do in case of Experiment I, pouring each quantity of the liquid of the oleic acid by means of a pipette tube to get a retarding action.

c) Continue the mixing operation during 50 seconds and put the mixed substance into a crucible; and then insert a mercury thermometer into that substance.

d) The following works are done with the same method as that of Experiment I.

Results of experiment:

Fig. 32 shows the temperature-time diagrams corresponding to the various quantities of the oleic acid that were added, and Table 15 shows the results of measurements about those products.

Referring to those diagrams and also the results of measurements about their products, following items of comprehension have been reached.

a) In case of experiment No. 6, when there was no additive, the diagram became the *trapezoid type*³⁾ just as it was occurred in the previous experiment.

b) In case of experiment No. 7, when 0.2cc of oleic acid per 50g total quantity was added during mixing operation, the diagram appeared also the *trapezoid type*³⁾, but it was rather near to the *acute angular*³⁾ type that means more or less extending or prolonging of the setting time.

c) In case of experiment No. 8, when 0.5cc of oleic acid was poured during mixing operation, the form of diagram almost completely transformed to the *acute angular type*³⁾. The properties of the product were also more or less improved just as shown by the form of diagram. Saying in details, the hardness was dropped from 50 to 45 that is considered more suitable, and the elasticity advanced from 90 to 95.

d) In case of experiment No. 9, when 0.7cc of oleic acid was poured, the diagram transformed further to the typical *hemicircular type*³⁾, resulting very

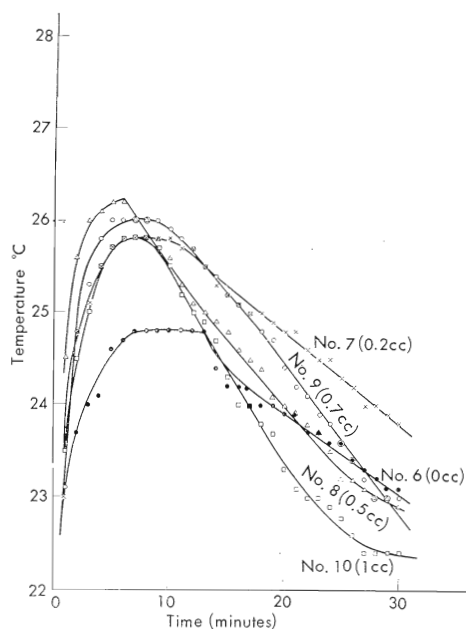


Fig. 32. Retarding method due to oleic acid

Table 15. Properties of the products, when oleic acid is employed as a retarder
 Conditions of experiments; Room temp.-19°C, Relative humidity...60%,
 Time used in mixing operation...50 seconds

Properties No. of Experiment	Hardness (Shore)	Elasticity (Shore)	Impression Surface	Form of Temp.-time diagram	Oleic acid added per 50 g
6	50	90	Fair	△	0 g
7	45	90	Fair	near △ (△)	0.2 cc
8	45	95	Fair	near △ (○)	0.5 cc
9	45	95	Fair	○	0.7 cc
10	45	95	Fair	○ near (○)	1 cc

suitable product as it would be imagined from the diagram.

e) In case of experiment No. 10, when 10 cc of oleic acid was poured, the diagram became the *hemicircular type*³⁾ of rather near to the *pseudo hemicircular type*³⁾, resulting somewhat dropping down of the quality of the product.

f) Considering from the preceding items, it may be said that retarding action due to the oleic acid was taken place very orderly paving each step of the grading in the classification of those temperature-time diagrams, as had been written in the author's earlier report⁹⁾. This very orderly caused transformation of diagram would perhaps be originated in the favorable dispersion of additive onto the mother substance, because of its fluidity.

EXPERIMENT III

On the retarding method due to the lead stearate

Method of experiment: The method of experiment on the retarding action due to the lead stearate was taken place with almost the same method as was done in the case of the stearic acid, namely the compositions of both A and B-agents, the method of the mixing operation, the method of adding of retarding agent, the treatment of the mixed substance, the measurement of the properties about the products and the others.

The only different point is that the quantities of A and B-agents being used in this case of experiment was 25g either against 50g either of the former case.

Results of experiment:

Fig. 33 illustrates the temperature-time diagrams corresponding to each amount of lead stearate added, and Table 16 shows the results of measurements about those products.

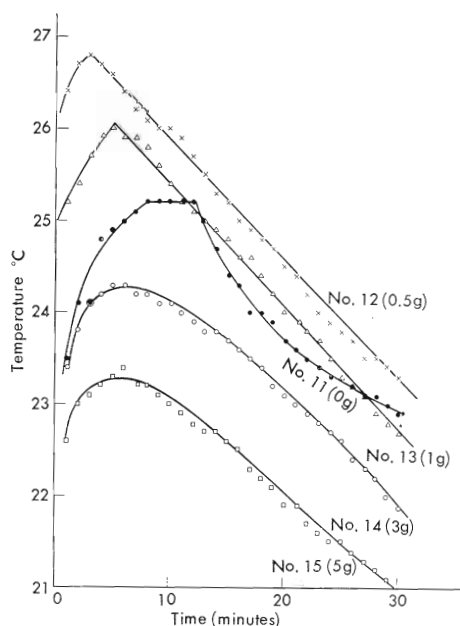







Fig. 33. Retarding method due to lead stearate

Table 16. Properties of the products, when lead stearate is employed as a retarder
 Conditions of experiments; Room temp...19°C, Relative humidity...60%,
 Time used in mixing operation...50 seconds

Properties No. of Experiment	Hardness (Shore)	Elasticity (Shore)	Impression Surface	Form of Temp.-time diagram	Lead stearate added per 50 g
11	55	90	Fair		0g
12	50	95	Fair		0.5g
13	50	90	Fair		1g
14	55	90	Fair		3g
15	55	90	Fair		5g

Referring to the diagrams and the results of the measurements into details, following items of comprehension have been reached.

a) In case of experiment No. 11, when no additive was mixed, the diagram appeared also the *trapezoid type*³⁾ as was in the previous experiments.

b) In case of experiment No. 12, when 0.5g per 50g total of the mother substance was added, the diagram transformed almost to the *acute angular type*³⁾, but it was rather near to the *trapezoid type*³⁾. Although, the product showed considerably improved results of measurements, namely the hardness changed from 55 to 50, and the elasticity from 90 to 95.

c) In case of experiment No. 13, when 1g of the lead stearate per 50g mother substance was mixed, the diagram showed the typical *acute angular type*³⁾, resulting a little drop in elasticity.

d) In case of experiment No. 14, when 3g of lead stearate per 50g total of the mother substance was mixed, the diagram transformed distinctively to the *hemicircular type*³⁾, but the properties of the product were rather taken back to the previous state, namely the hardness changed from 50 to 55 and the elasticity from 95 to 90.

e) In case of the experiment No. 15, when 5g of lead stearate was added, either in the form of diagram or in the properties of the product, there was no distinctive difference compared to the case of No. 14, except the lowering of the summit point in some degrees.

f) Considering from the preceding items, it may be concluded that though the retarding action due to the lead stearate was taken place very regularly, the amounts exceeding 1g of the lead stearate per 50g total of the mother substance would result the considerable dropping in quality.

DISCUSSION AND SUMMARY

Table 17 describes about the comparisons among the above mentioned three retarders that have been brought into the examinations heretofore. The following items are the explanations about that.

Table 17. Comparison of retarding action

Retarders	Stearic Acid	Oleic Acid	Lead Stearate
Retarding capability due to 1g or 1cc per 100g mother substance	$\triangle \rightarrow \triangle$ $\rightarrow \bigcirc$ $\rightarrow \bigcirc$ $\rightarrow \square$	$\triangle \rightarrow \triangle$	$\triangle \rightarrow \triangle$ (\triangle) near
Best amounts per 100g mother substance	Less than 1g	1.4 cc	1 g
Limit of utilization per 100g mother substance	1 g	3 cc	2 g

a) *Retarding capacity*

The most capable retarder among those reagents was, of course, the stearic acid. Its only 1g addition has resulted the transformation of the temperature-time diagram crossing three steps of grading, namely from the *trapezoid* to the *satrant type*³⁾. In the case of oleic acid, 1cc adding of it resulted the transformation of the diagram on the only one step of the grading. Further more, in case of the lead stearate, the diagram, too, transformed just like as in the case of the oleic acid, when compared 1g of lead stearate to 1cc of oleic acid. However, saying in details, the transformation due to the 1g of lead stearate was rather slighter than the case due to the 1cc of oleic acid, because the *acute angular type*³⁾ due to the lead stearate was rather near to the *trapezoid type*³⁾.

b) *Best amounts per 100g mother substance*

If we wish to obtain a suitable products of those impression materials, we must remember the most appropriate amounts of such retarders in practice. The best amounts of such retarders were roughly estimated just as written in the Table 17, considering from the results of experiments.

c) *Limit quantities in utilization*

We must especially remember the limit quantities of those retarders that mean the amounts not to exceed because of the protection of keeping the good quality of the mother substance, namely the polysulfide rubber impressions. The quantities written in Table 17 were concluded for each retarder, referring to the results of the preceeding experiments.

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