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Project NY 430 030-8.02
Technical Note N-303
14 June 1957

INTERIM REPORT ON HYDROPHOBIC CEMENT

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Port Hueneme, California

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INTERIM REPORT ON HYDROPHOBIC CEMENT

D. F. Griffin and W. R. Lorman

OBJECT OF PROJECT

To provide for investigations leading to the development of improved materials, design criteria, and construction techniques in the field of portland cement concrete.

OBJECT OF SUBPROJECT

To investigate methods for effecting savings of portland cement in naval shore establishment construction.

OBJECT OF TASK

To determine the effectiveness of oleic acid in preventing hydration of portland cement during transit and storage; to find an air-detraining agent to be incorporated in oleic acid-treated cement; and to establish the relationships among humidity, fineness of cement particles, strength of mortars and concretes, and optimum quantities of oleic acid and an air-detraining agent.

OBJECT OF THIS REPORT

To show results of investigations made to disclose why commercially produced hydrophobic cement failed to meet the task objective, and to recommend future courses of action which may meet the task objective.

RESULTS

Presumably, tri-n-butyl phosphate, an air-detraining agent, reacts with oleic acid-treated cement to form either calcium phosphate or calcium butyl phosphate. Such reactions prevent tri-n-butyl phosphate from acting as an air-detraining agent when used as an additive; however, it may be used successfully as an admixture.

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SUMMARY

~~The Bureau of Yards and Docks requested the laboratory~~ to determine the effectiveness of oleic acid in preventing hydration of portland cement during storage and transit, and to seek an agent that could be incorporated with oleic acid-treated cement to reduce air entrainment (caused by oleic acid) in plastic mortars and concrete.

Experiments were made to incorporate tri-n-butyl phosphate with cement at various locations in a commercial production plant conveyor system. The entrained air contents of mortars made with the cement thus produced were not lowered by the tri-n-butyl phosphate.

It ~~was subsequently discovered that~~ tri-n-butyl phosphate reacts with oleic acid-treated cement to form either calcium phosphate or calcium butyl phosphate, deactivating the tri-n-butyl phosphate as an air-detraining agent. Elevated temperatures of the cement during the production runs accelerated the chemical reaction (or reactions). The same reaction took place at usual room temperatures over longer periods of time. Hence, little would be gained by cooling the cement in storage before incorporating tri-n-butyl phosphate.

Further tests will be conducted to find an air-detraining agent that will remain inert when added to hydrophobic cement at elevated temperatures up to 250 degrees Fahrenheit.

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INTRODUCTION

The hydrophobic cement task was begun by U. W. Stoll and reported in Technical Note N-229,[1] dated 6 September 1955, indicating that oleic acid treatment of cement is economically feasible, and that tri-n-butyl phosphate added to oleic acid-treated portland cement will reduce the air-entrainment caused by oleic acid. Thus, hydrophobic cements could be developed to make hardened mortars and concretes with strengths to approximate those made from undeteriorated hydrophilic cements.*

*Hydrophobic cements have a higher degree of resistance to deterioration caused by atmospheric moisture than do hydrophilic cements.

Cement containing oleic acid and tri-n-butyl phosphate was developed at the Laboratory, and a contract was negotiated with the Riverside Cement Company, Los Angeles, California, on 29 May 1956 to produce a similar material on a commercial basis. This company regularly produces oleic acid-treated cement, and it appeared to be a simple matter to add tri-n-butyl phosphate into the production system where it could be mixed thoroughly with the cement before reaching the sacking machine.

Riverside Cement Company made its first production run at its Crestmore Division Plant on 6 June 1956. About 200 sacks of cement were produced, each containing 0.07 per cent by weight of oleic acid and 0.05 per cent of tri-n-butyl phosphate. A second run of equal magnitude was made on 13 June 1956. Several tests of mortars made with samples of cement from both runs revealed air contents of about 24 per cent by volume. These excessively high values indicated that the tri-n-butyl phosphate was not active as an air-detraining agent. Several tests subsequently were performed at the Laboratory to find out what deactivated the tri-n-butyl phosphate. A description of the tests and their results are a primary part of this report.

Research from June 1956 through September 1956 was under the technical direction of W. R. Lorman, under the cognizance of D. F. Griffin. Investigations since September 1956 were made under the technical direction of D. F. Griffin, with consulting services of W. R. Lorman.

Statement of the Problem

Hydrophobic cement is portland cement that has a high degree of resistance to hydration when exposed to atmospheric water vapor. The comparative degree of resistance may be observed visually by separately storing hydrophobic and hydrophillic cements in open pans in highly humid conditions at room temperatures. Hydrophilic cements become quite lumpy within a matter of days due to hydration. Hydrophobic cements remain soft and smooth without lumps for longer periods of time. Positive proof that hydrophobic cements do not become partially hydrated while remaining free of lumps is lacking. Another test, the float test, also demonstrates the hydrophobic character of cement. Hydrophobic cement floats when sprinkled over the surface of water; type I portland cement sinks immediately.

One method of producing hydrophobic cement is by intergrinding oleic acid with portland cement clinker. The monomolecular film of fatty acid thus formed about each cement particle, acts as a water vapor barrier to retard hydration. This film is broken under the abrasive action of aggregates during mixing of mortars and concretes.

Oleic acid also acts as an air-entraining agent in mortars and concretes. A mortar made with normal portland cement containing 0.10 per cent oleic acid by weight exhibits an air content of about 24 per cent by volume. Mortars made with normal portland cements with no oleic acid usually have air contents of about 7 per cent.

The high air content of mortar made with hydrophobic cement is responsible for a decrease in compressive strength of hardened mortar cubes compared to the strength of mortar cubes made with hydrophilic portland cement.

PROCEDURE

Commercial Production

Tri-n-butyl phosphate was added to the cement at the discharge end of the finish-grind ball-mill during the first production run of hydrophobic cement. High air contents in mortars made with this cement at first were believed to have resulted from a substantial loss of tri-n-butyl phosphate through the dust collector system.

During the second production run of hydrophobic cement, tri-n-butyl phosphate was introduced at the feed end of the finish-grind ball-mill. High air contents of mortars made with this cement were believed to have occurred because of: (1) loss of tri-n-butyl phosphate through its adherence to the surface of the steel balls and to the inside surface of the ball-mill, (2) thermal effects of the hot cement (up to 250 degrees Fahrenheit) on the tri-n-butyl phosphate, and (3) loss of tri-n-butyl phosphate through the dust collector system.

Optimum TNBP and Oleic Acid

Several tests subsequently were performed to determine the optimum quantity of tri-n-butyl phosphate. For this purpose Riverside Plastic Cement (type I with 0.10 per cent oleic acid by weight interground) was used as the control. Mortar made with this cement usually has about 24 per cent entrained air by volume. The air contents for this series of tests were determined according to American Society for Testing Masterials, Designation C 185-55T.[2] Supplementary tests were made with a special grind of Riverside cement clinker and 0.30 per cent by weight of oleic acid. Test results* are given in Table I and shown in Figure 1.

*As a further check, similar results were obtained using oleic acid-treated cement made in the Laboratory from Victor cement clinker.

Table I. Air contents of mortars made with oleic acid-treated cement and various percentages of tri-n-butyl phosphate

TNBP per cent by weight	0.1 per cent Oleic Acid[1]	0.3 per cent Oleic Acid[2]
0	23.9	24.9
0.02	15.7	18.8
0.04	11.0	--
0.06	9.2	14.6
0.08	8.2	--
0.10	8.3	12.2
0.12	8.1	--
0.14	7.8	--
0.16	8.0	11.8
0.18	7.8	--
0.20	7.6	11.7
1.00	7.2	--
2.00	7.1	--
3.00	7.1	--

(1)Riverside Plastic Cement, average of 3 tests each.
(2)Jar mill grind of Riverside Cement Clinker, individual test results.

Variations in individual test values for a given percentage of tri-n-butyl phosphate were insignificant. The economically optimum amount of tri-n-butyl phosphate either for Riverside Plastic Cement containing 0.10 per cent oleic acid or 0.30 per cent oleic acid is between 0.08 and 0.10 per cent by weight of cement. Very little additional air-detrainment can be obtained by using more than 0.09 per cent of tri-n-butyl phosphate.

It was concluded that sufficient tri-n-butyl phosphate had been included in the production runs to effect some air detrainment. Thermal effects were therefore indicated as being the chief cause of deactivating the tri-n-butyl phosphate as an air-detraining agent.

Thermal Effects

Samples of Riverside Plastic Cement were heated to temperatures of 240.8, 199.4, 159.8, and 120.2 degrees Fahrenheit, respectively. Tri-n-butyl phosphate at about 78 degrees Fahrenheit was blended mechanically with the various samples of hot cement in the amount of 0.06 per cent by weight. The treated samples immediately were stored in sealed containers until their temperatures dropped to room temperature.

Average air contents were found to be 8.9, 8.9, 8.9, and 8.3 per cent by volume, respectively, for each of the mortars incorporating cements that had been exposed to respective temperatures of 240.8, 199.4, 159.8, and 120.2 degrees Fahrenheit. Each mortar tested involved three separate batches. These results indicated that thermal effects should be investigated for longer exposures to elevated temperatures.

Additional samples of Riverside Plastic Cement were heated for various time intervals at a constant temperature of 240.8 degrees Fahrenheit. At the end of specific time intervals the samples were mixed with 0.10 per cent by weight of tri-n-butyl phosphate, also at a temperature of 240.8 degrees Fahrenheit. Immediately after mixing, each sample was stored in a sealed container and allowed to cool to room temperature. Results of air content determinations on mortars made with these samples are tabulated below, as averages for three samples each:

Hours of Exposure of Cement and TNBP Separately to 240.8°F	Air Content of Mortars per cent by volume
1	9.1
2	8.4
4	8.1
8	7.9

An experiment similar to the above was carried out which involved heating only the tri-n-butyl phosphate and not heating the cement. The hot tri-n-butyl phosphate was added to the cold cement in the amount of 0.10 per cent by weight and thoroughly mixed. Air content determinations on mortars made with these samples are shown below as averages for three samples each:

Hours of Exposure of TNBP to 240.8°F	Air content of Mortars per cent by volume
9	10.7
10	10.4
12	10.7
16	10.3

Although these data indicate that heating the tri-n-butyl phosphate for periods longer than 8 hours reduces its air-detrainment properties, heat was not concluded to be the cause of its complete loss of effectiveness in the production runs.

A final series of tests was made by heating a mixture of Riverside Plastic Cement and 0.10 per cent tri-n-butyl phosphate for various exposure periods and at various constant temperatures. Upon removal from the oven, treated cement samples immediately were placed in sealed containers and allowed to cool to room temperature before air content determinations of mortars were made. The results* are given in Table II and are shown in Figure 2. These data indicate that heating the dry combination of cement, oleic acid and tri-n-butyl phosphate induces a chemical reaction that reduces the air-detrainment properties of tri-n-butyl phosphate. The precise nature of the chemical reaction is not known.

*Similar results were obtained using oleic acid-treated cement made in the Laboratory from Victor cement clinker.

Intergrinding oleic acid with portland cement clinker may produce calcium oleate. The tri-n-butyl phosphate when mixed with the cement may produce a calcium phosphate or calcium butyl phosphate. Such chemical reactions deactivate the tri-n-butyl phosphate as an air-detraining agent.

A rule-of-thumb sometimes used to determine magnitudes and rates of chemical reactions at various temperatures is that the rate of reaction doubles for every 10 degrees centigrade rise in temperature. On this basis it was predicted that the above-described reaction would take place in a matter of months if the tri-n-butyl phosphate were added to cold cement instead of hot cement as in the previously discussed commercial production runs.

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Table II. Air contents of mortars made with Riverside Plastic Cement intermixed with 0.10 per cent tri-n-butyl phosphate and exposed to variables of temperature and time (individual tests).

Hours of Exposure	Temperature in degrees Fahrenheit 240.8	199.4	159.8	120.2
0	8.9	8.9	8.9	8.9
1	12.6	--	--	--
2	15.3	11.6	9.0	9.1
3	17.1	--	--	--
4	18.0	14.1	9.4	8.7
5	19.4	--	--	--
6	20.1	--	--	--
8	--	17.1	9.9	8.5
9	21.2	--	--	--
12	22.2	--	--	--
15	23.6	--	--	--
16	--	19.1	10.9	8.5
18	23.6	--	--	--
20	--	19.9	10.7	8.1
21	23.7	--	--	--
24	23.3	20.8	10.8	8.3

In order to verify the magnitude and rate of the chemical reactions at ordinary room temperature, several samples of Riverside Plastic Cement were stored in sealed cans in the 50 per cent relative humidity room at constant temperature of 73.4 degrees Fahrenheit. Several additional samples of Riverside Plastic Cement with 0.10 per cent tri-n-butyl phosphate intermixed were also stored in the 50 per cent relative humidity room. Air contents of mortars made with these samples at regular time intervals are as follows:

Air Content in per cent by volume of Riverside Plastic Cement Mortars containing 0.10 per cent Oleic Acid (average of 3 tests each):

Cement Without TNBP	Elapsed Time Days	Cement with 0.10 per cent by weight TNBP
26.3	0	8.7
26.0	30	12.9
26.0	60	18.3
26.6	91	21.6
26.5	119	22.1
26.5	150	22.4
26.1	181	22.9
25.5	212	23.1

The above data clearly verify the rule-of-thumb prediction. Within four months chemical reactions took place in the oleic acid-treated cement with tri-n-butyl phosphate that virtually deactivated the latter as an air-detraining agent. Consequently, it is concluded tri-n-butyl phosphate may be satisfactory as an air-detraining admixture* but not as an air-detraining additive.*

*Admixture means adding at the time of mixing. Additive means incorporating during manufacture.

PLANS

Experiments will be made with various chemicals to find one that will remain inert when used as an additive, and that will act as an air-detraining agent when the oleic acid-treated cement is mixed into plastic mortars and concretes. In addition a comprehensive series of tests will be made to compare strengths of concretes and mortars made with oleic acid-treated cement and type I portland cement, each exposed to various conditions of humidity and temperature for various periods of time.

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REFERENCES

1. NAVCERELAB Technical Note N-229, Hydrophobic Cement, By U. W. Stoll, 6 September 1955.

2. ASTM Standards, Part III, American Society for Testing Materials, 1955.

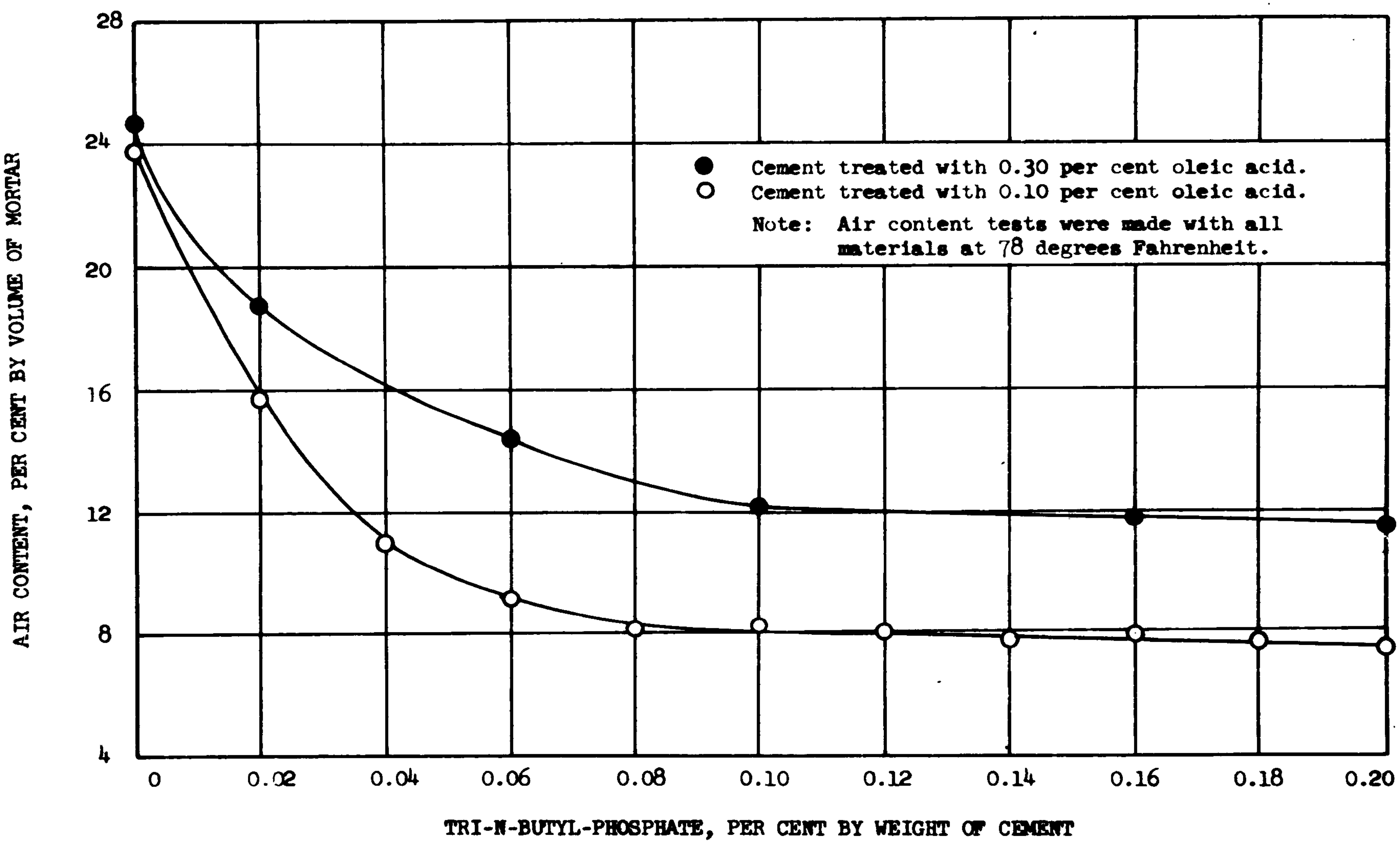

Figure 1. **Relationship between air content and amount of tri-n-butyl-phosphate in Riverside Plastic Cement mortars.**

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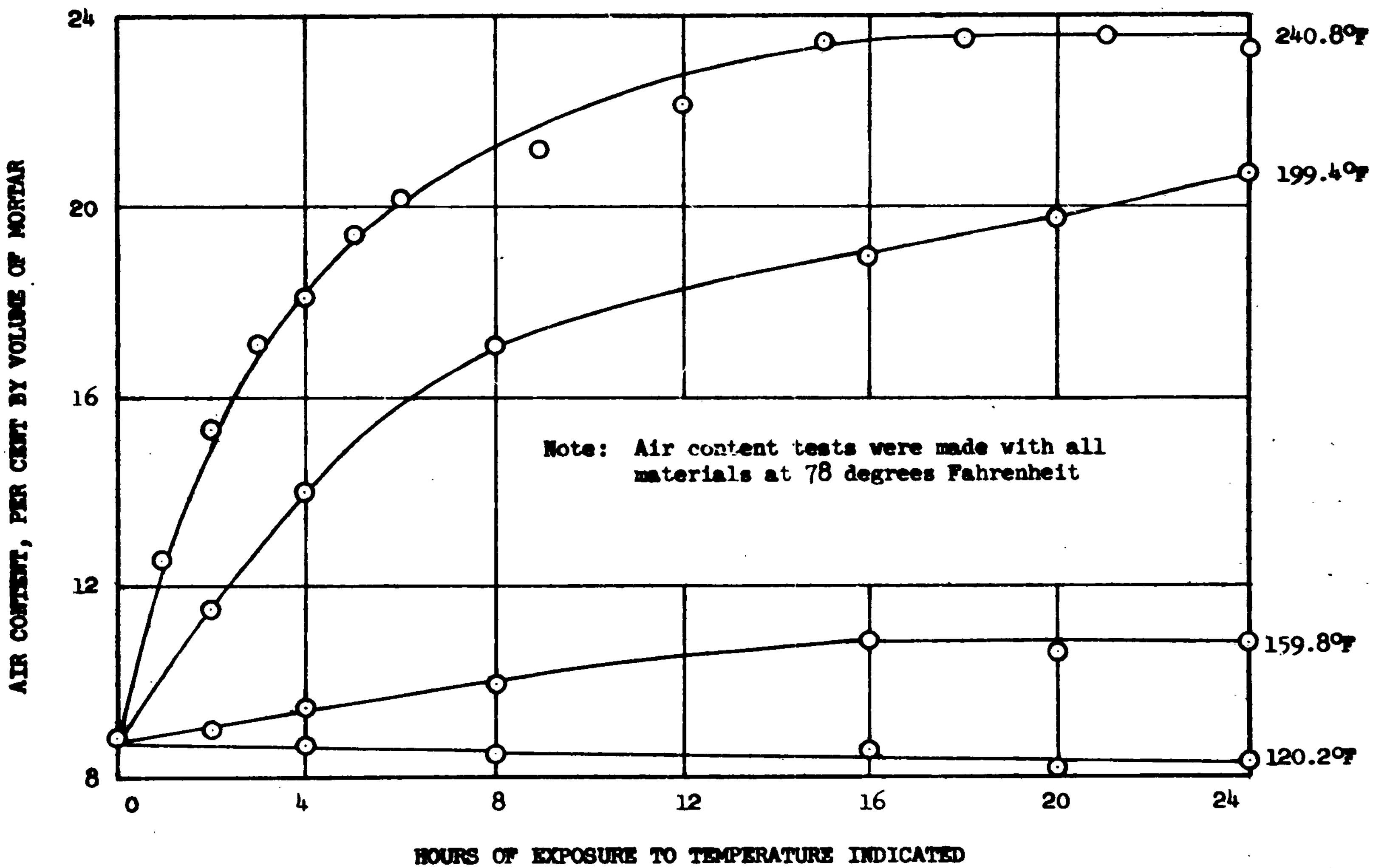

Figure 2. Effect of heat on air-entrainment properties of Riverside Plastic Cement with 0.1 per cent tri-n-butyl-phosphate by weight intermixed.

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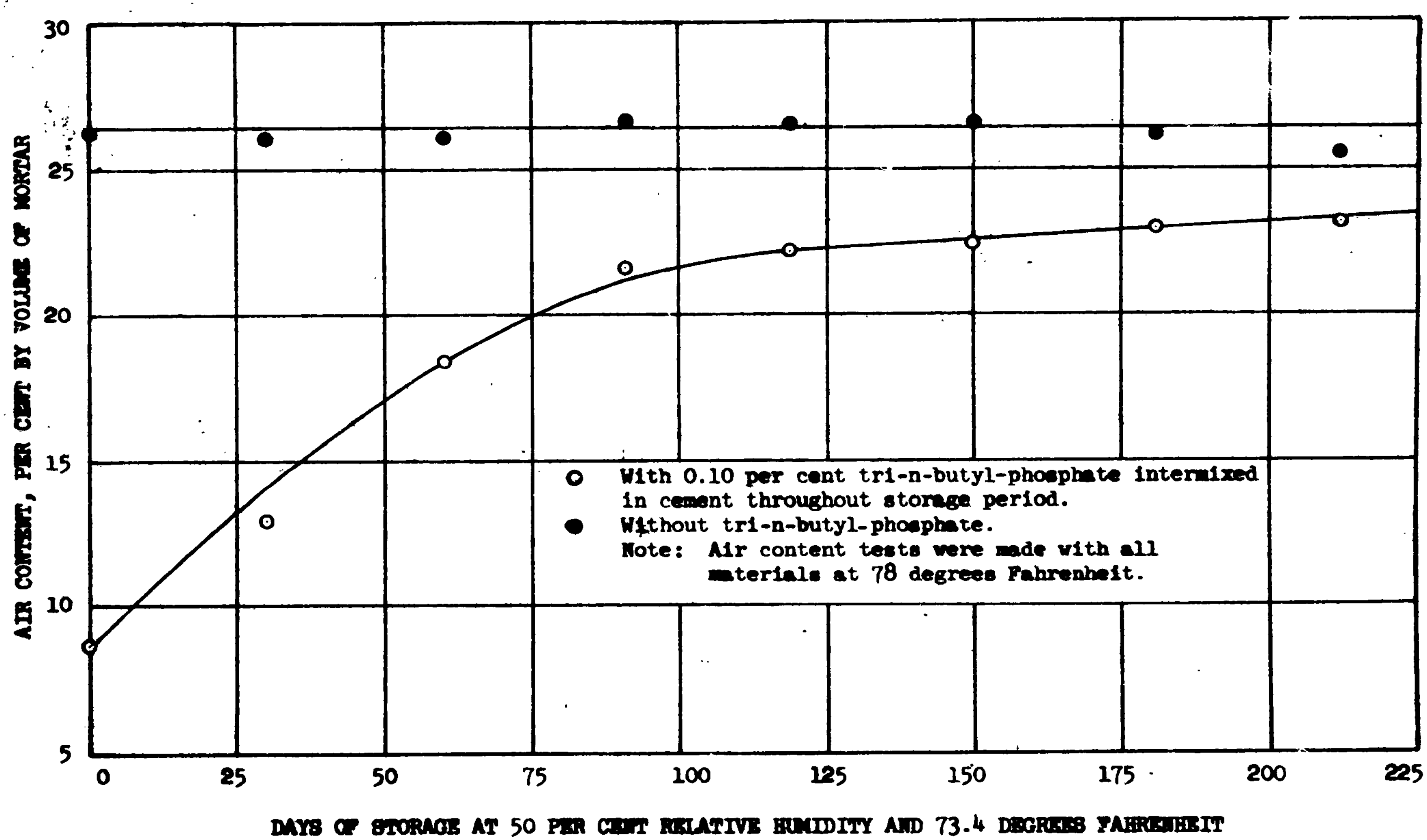

Figure 3. Effect of tri-n-butyl-phosphate and long-term storage at room temperature on air-entrainment properties of Riverside Plastic Cement.