United States Patent Office 3,034,909 Patented May 15, 1962

3,034,909

SELF-RELEASE ADHESIVES

Robert H. Sams, Aldan, and Claire H. Jeglum, Swarthmore, Pa., assignors to Philadelphia Quartz Company, Philadelphia, Pa., a corporation of Pennsylvania

No Drawing. Filed Dec. 11, 1958, Ser. No. 779,567
9 Claims. (Cl. 106—80)

INTRODUCTION

This invention generally relates to a method for decreasing the adhesion of silicate adhesives to heated metallic surfaces. More particularly, this invention involves incorporating organic amyl phosphates in combination with other additives in silicate adhesives so as to decrease the metal adhering properties of the silicate adhesive.

THE PROBLEM

In the production of a laminated paperboard the adhesive is applied to the surface of one sheet and a second sheet is pressed over the adhesive layer and held in the laminated position until the adhesive has set primarily by loss of moisture. In the manufacture of corrugated paperboard for example, the adhesive is applied to the tips of the corrugations and a liner sheet is applied in position in contact with the flute tips of the corrugation. The adhesive is then dried by passing the web over heated metal plates called platens in the case of the double-backer or a heated roll in the case of the single-face liner. In the practice of this process the laminated sheets may become misaligned and the adhesive on the flute tips at the edge of the web may be scraped off onto the hot metal surfaces or if too heavy a glue spread is applied some may ooze from the edge of the combined sheet and drip onto the hot platen. The adhesive may also come into contact with the hot metal surfaces if a liner sheet breaks and the unprotected flute tips come into direct contact with the platen.

Soluble silicates readily attach themselves to metal surfaces. They are polar adhesives and form a strong bond with the metal when dried out. Furthermore, the dry silicate adhesive itself is strong and hard and glassy. Ridges and rough spots formed by the dried adhesive will scratch the outer surfaces of the laminated boards in passing over them. It is therefore necessary for the operator to remove the hard drippings and accumulation first by chipping them off by hand and then by scraping and polishing the metal surface to restore it to its original smooth condition. This cleaning operation is slow and tedious and must be understaken 2 or 3 times a day in some cases depending on the ability of the operator to schedule board of increasingly narrow width and to avoid accidents to the paper liner. Silicate adhesives nevertheless continue to be used by the corrugating industry particularly where board having extra strength and rigidity is desired. Oil coatings on metal rollers and graphite coatings on metal aprons to reduce scraping have been of some assistance.

A solution to the silicate clean-up problem has been sought for over twenty years. Generally, two approaches have been taken. One is to provide a protective coating for the metal surfaces which may become smeared with silicate. However, a satisfactory coating must not only be silicate-resistant but must withstand temperatures up to 400° F. as well as vigorous wear of the paper sheet passing over it continuously. The second approach is to modify the adhesive itself with additives. However, a satisfactory additive must not only be an effective parting agent toward metal, but must be compatible with the silicate adhesive, add little to its cost or odor and not interfere with its intended purpose of gluing paper. Consideration has also been given to changing the metal of which the corrugating equipment is constructed but even if a satisfactory solution were found in this way, it would be difficult to have it accepted by the manufacturers of such equipment.

It has long been known that surface active agents may be added to sodium silicate solutions to increase the wetting property in various industrial uses. In general, surface active agents are of little benefit in increasing the ease of wetting by soluble silicate adhesives. They also tend to increase the viscosity of the solution and are more expensive than the silicate while tending to reduce the tensile strength of the bond to paper. It has also been known that 0.5% isoamyl orthophosphate added to "N" sodium silicate will reduce the adhesion to metal but not sufficiently to be practical.

We have investigated several hundred additives for their effect on the ease of separation of the soluble silicate adhesives from the hot metal surface. Prior to the discovery of this invention, the best material we had found was the condensation product of a rosin ester with maleic anhydride. Maleic anhydride is an unsaturated organic compound with a high dipole moment. The condensate with rosin has the highest possible ratio of carboxyl groups per molecule. However, the melting point of the sodium salt is far above the temperature of the hot metal platen. While the use of this material did receive some industrial acceptance, it added to the cost of the adhesive and required at least a gentle tap to remove lumps from the hot surface.

A number of prior art patents have dealt with this problem, as for instance, Nos. 2,347,419; 2,671,747; 2,736,678; 2,772,177; 2,788,285; and 2,834,744.

OBJECTS

The main object of the present invention is to provide a composition and method for decreasing the adhesion of an adhesive silicate composition to heated metal surfaces generally. These and other objects will occur to those skilled in the art from the description of the invention set forth below.

THE INVENTION BROADLY

We have discovered that by incorporating a combination of an isomer of an amyl ester of phosphoric acid with one chemical compound selected from the group of urea and sugar and/or one chemical compound selected from the group consisting of triethanolamine and "Mersize" (a trademarked product of the Monsanto Chemical Company comprising a condensation product of rosin and maleic anhydride) with a silicate adhesive we can obtain a good corrugated board bond and yet any adhesive which is spilled and dries on the heated plates of the corrugator is more easily removed than any other silicate adhesive modified in any other known manner.

THE SILICATE ADHESIVE

We have found that any sodium silicate type adhesive can be used in accordance with this invention. As is well known, aqueous sodium silicate alone forms highly satisfactory adhesive materials. It is therefore contemplated that simple combinations of aqueous sodium silicate, an organic amyl phosphate with urea or sugar or triethanolamine or "Mersize" can be produced in accordance with this invention. Likewise, as is well known in the prior art, a considerable number of "additive" compounds may be combined with aqueous sodium silicate in order to produce a useful modified silicate adhesive. This invention contemplates incorporating organic amyl phosphates and at least one from the suggested groups in these modified silicate adhesives in order to decrease the metal ad-

hering properties of the adhesive. Specific examples of such modified silicate adhesives can be found in Patents Nos. 2,239,358; 2,554,035; 2,669,282; 2,772,996 and 2,681,290.

Especially preferred silicate adhesives which may be used as a base in this invention range in weight ratio of SiO_2 to Na_2O from about 2 to 4. These silicates may have from 35 to 45% solids content. They may be combined with up to 10% starch, up to 20% clay, up to 10% urea, up to 2% triethanolamine, up to 10% sugar, up to 2% "Mersize" and other materials commonly added to silicate adhesives.

THE ORGANIC AMYL PHOSPHATES

Specific examples of simple isomers of amyl esters of phosphoric acid which are included within the scope of this invention are as follows:

(1) Amyl acid phosphate
(2) Monodiamyl acid phosphate
(3) Monodi-iso-amyl acid orthophosphate
(4) Mono-iso-amyl acid orthophosphate

It is prefeerred that the organic amyl phosphates be incorporated in the silicate adhesive in an amount ranging between 0.25 and 2.0% of the silicate adhesive.

THE GROUP SUGAR AND UREA

While it has been known that 5% or more of urea will decrease resistance to separation of silicate adhesive from hot metal, this decrease, as shown below, has not been sufficient for practical use. Urea combined with other materials is more effective and we have now found that when combined with an organic amyl phosphate, even less than 5% of urea will provide silicate adhesives which separate at practical resistance levels. We have found that for practical purposes ordinary cane sugar may be substituted for urea.

THE GROUP MERSIZE AND TRIETHANOLAMINE

While it has been known that addition of from about 0.1 to 2% of triethanolamine or Mersize to silicate adhesives will decrease resistance to separation from hot metal, again, the decrease has not resulted in product acceptance and we now find that when coupled with one of the organic amyl phosphates, there is a synergistic decrease in the resistance to separation.

Furthermore we find the very best results when we combine the organic amyl phosphate, the urea or sugar, and the triethanolamine or Mersize in one silicate adhesive having the approximate range of 1 to 5% of urea or cane sugar, 0.1 to 2% triethanolamine or Mersize, 0.2 to 2% of organic amyl phosphate, 0 to 20% of clay, 0 to 10% commercial starch and the remainder substantially soluble silicate solution having a ratio of SiO_2 to Na_2O of 2 to 4 at a concentration permitting machine application satisfactory for the purpose in hand. The preferred range of organic amyl phosphate is 0.25 to 1%.

METHOD FOR TESTING DEGREE OF ADHESION TO METAL

There are a number of ways in which the additives for a silicate adhesive may be tested. First, there is the visual comparison in which the adhesive mixture is allowed to dry on a surface heated to the ordinary platen or hot plate temperature of the corrugating machine. The dried silicate puffs up and the blob or coating is chipped off manually. A blob of "N" silicate heated in this manner would be so hard that a metal instrument is needed to drive off and scrape away the residual adhesive. A good self-releasing adhesive can be knocked loose with a piece of stiff cardboard or liner board such as is used for manufacturing corrugated boxes and the residue rubbed away with the surface of a liner board. This manual testing method gives a rough comparison

but it is difficult to compare the precise relative metal adhering values of materials in this manner.

A more precise testing procedure is described in an article entitled "Adhesion of Sodium Silicate to Metal" by John H. Wills and Robert H. Sams, published in TAPPI, July 1950, page 83A. In this test procedure, the puffed silicate residue was formed on the hot plate and then the resistance to crushing or shear was obtained by forcing a blade through the honey-combed structure just above the interface between the metal and the dried film. This resistance is shown as Table I in the reprint.

A still better method of determinating the clean-up resistance quantitatively was developed in our laboratory. In this method a paper cylinder 0.5 inch high having an I.D. equal to that of a nickel (2.0 cm.) was placed upright on the hot plate surface. A piece of wire shaped to form a flat coil with a loop rising above its center and having the outside diameter of a penny (1.8 cm.) was rested on the hot plate within the paper cylinder or well. About ⅛ inch depth of adhesive was poured into the paper well, around and over the coil of wire. After the adhesive became thoroughly baked at the 350° F. temperature of the hot plate (20 minutes were allowed) the force in pounds required to lift the wire and its surrounding adhesive crust from the hot plate surface was measured with a push-pull gauge. The wire loop was cleaned before reuse. With this method the following results were obtained:

	Clean-up resistance (in lbs.)
"N" sodium silicate	7.5
97 "N" sodium silicate, 1% Mersize, 2% urea	2.1

("N" sodium silicate has a gravity of 41° Bé. and a ratio of one part of Na_2O to 3.22 parts of SiO_2. "Mersize" is a condensation product of rosin and maleic anhydride.)

In a series of tests in which a sugar was substituted for the urea, it was found that while commercial sugar had considerable effect in aiding clean-up, it was somewhat less effective than urea. Also, when triethanolamine was substituted for Mersize, the results were nearly as good. It is more miscible with the silicate and foams less.

PRELIMINARY TREATMENT OF THE METAL

The very best separation from a metal surface has been produced using our special adhesive with a specifically prepared silicone film on the surface of the metal as described in Example 4. Other surface coating materials have shown good separation but have not been as resistant to wear.

Such other coatings which showed satisfactory release of hot silicate residue and some appreciable resistance to wear were "Teflon" (polytetrafluoroethylene) coverings and a waxy chromate. Also, mixtures of 1 part of organic phosphate and 2 parts of turpentine gave satisfactory resistance to the silicate but unsatisfactory resistance to wear. The same organic phosphates which were used as additives showed better than normal effectiveness as a coating material.

EXAMPLES

The following examples are illustrative of some preferred embodiments in accordance with this invention. It should be understood that these examples are not intended to limit the invention and that obvious changes may be made by those skilled in the art without changing the essential characteristics or basic concepts of the invention. The parts and percentages are by weight unless otherwise indicated.

Example 1

A 41° Bé. solution of sodium silicate (having a ratio of $1Na_2O:3.22SiO_2$) was prepared for use as an adhesive. When tested according to the previously described wire hook procedure this material was found to have a clean-up resistance of 7.5 lbs.–9.5 lbs.

Example 2

When the sodium silicate adhesive of Example 1 was modified by the addition of 0.5% mono-isoamyl acid orthophosphate (referred to as phosphate) and the resistance to removal of the dry film was compared, it was found that while the phosphate did increase the ease of removal of the silicate film, it was not as satisfactory as when Mersize was used alone. Similarly, when 2% urea was used with the silicate adhesive of Example 1 removal of the dried film was no easier than with the Mersize additive, but a mixture of 2% urea and 1% of Mersize or triethanolamine in the silicate did improve the ease of removal. If corn sugar was used in place of urea the dry film was nearly as easy to remove.

When 1% of Mersize and 0.5% phosphate were added to the silicate adhesive there was considerable improvement over the prior mixtures and when a combination of 96.5% "N," 1% Mersize CD–2, 2% urea, and 0.5% of phosphate was used, the dry cake came away quite cleanly at a very light touch and was decidedly easier to remove than the combination of 1% Mersize, 2% urea and 97% "N" which required a removal force of 2 to 3.

Adhesive	Viscosity Stormer seconds	Pull, lbs.
"N"	43.5	9.5
"N"+0.5% phosphate+2% H_2O	53.4	3.0
"N"+1% Mersize	44.3	5.1
"N"+2% urea	42.5	6.0
"N"+1% Mersize+0.5% phosphate+2.5% H_2O	51.0	2.3
"N"+2% urea+0.5% phosphate+3% H_2O	43.8	2.3
"N"+1% Mersize+2% urea	45.1	3.1
"N"+0.5% phosphate+1% Mersize+2% urea+3.2% H_2O	42.5	about 1.5

Example 3

A first (#1) commercial silicate adhesive was prepared having the following composition:

7% of pearl starch
77.5% of "N" sodium silicate
8.5% of Barden air-classified clay
7.0% of water

A second (#2) modified commercial silicate adhesive was made having the following composition:

0.5% monoiso-amyl acid orthophosphate
0.1% of NaOH
1.5% of industrial crystal urea
0.5% of technical triethanolamine
75.0% of "N" sodium silicate
7.0% of pearl starch
8.5% of Barden air-classified clay
6.9% of water

From the above it will be seen that 2.5% of the "N" sodium silicate content of adhesive #1 was replaced with 2.5% of four other ingredients in order to produce #2. The viscosity of adhesive #1 at 75° F. was 53.4 Stormer seconds and the viscosity of adhesive #2 at 75° F. was 93.4.

In order to compare the relative adhesion of the above adhesives to hot metal, a laboratory hot plate was used to heat a sheet of stainless steel 0.0833 inch thick. The sheet was cleaned by abrasion and then adjusted so that the sheet temperature rose to a maximum of about 340° F. in about 10 minutes. The previously described testing procedure with the wire hook was used. The strength required to lift the adhesive from the stainless steel sheet was 6.8 pounds for adhesive #1 but only 1.4 pounds for adhesive #2.

Example 4

A further test was made using coatings of F–121 silicone solution (25% silicone solids in VM & P Naphtha, reference 5–203, November 1954). The coating solution contained 4 parts of F–121 silicone fluid, 6 parts of naphtha, 0.5 part of powdered aluminum (to increase the visibility of the film), 2 parts of Catalyst XY–26 (lead 2-ethylhexoate solution). The stainless steel sheet was first cleaned by abrasion and then the F–121 silicone coating solution was applied with a soft brush. After an hour of air-drying the coated steel sheet was placed on a warm hot plate to heat the surface quickly to 340° F. A half hour after the warming began, the coated area was rubbed 100 times with a piece of kraft liner. Then the lift resistance of adhesive #1 of Example 3 from the coated area was determined immediately. A short time later, the lift required by adhesive #2 of Example 3 was determined on an adjacent part of the coated area.

In this case the lift resistance of adhesive #1 was only 1.1 pounds. The adhesive #2 was less than 0.1 pound. Actually, in some later cases it was found that adhesive #2 separated voluntarily from the special coating.

Example 5

A standard formula was prepared which contained:

0.5% organic phosphate
1.9% water
0.1% NaOH
1.5% urea
0.5% triethanolamine
95.5% "N" sodium silicate

All of the ingredients except the silicate were combined to form a clear, thin solution and then the silicate was agitated vigorously while the solution was added to it. After the mixing foam had subsided the adhesives were tested for the regular Stormer viscosity at 75° F., also for hot plate clean-up resistance in pounds and for the strength in pounds of B-flute bond specimens prepared with the adhesives and conditioned for at least two days. The B-flute bond test was made with the standard Thwing-Albert electro-hydraulic tensile tester flute bond measuring equipment.

In the following table variations of the standard formula are indicated under composition.

Composition	Viscosity (Stormer secs.)	Clean-up (lbs.)	Bond strength (lbs./ft.)
100% "N" silicate	43.5	7.5	36
No organic phosphate 96% "N"	31.3	4.8	28
The amyl phosphate was amyl acid phosphate	55.2	2.0	34
Amyl acid phosphate with urea increased to 3% and "N" reduced to 94%	61.7	1.5	33
Monodiamyl acid phosphate	51.3	2.2	29
Monodi-iso-amyl acid orthophosphate	55.3	2.7	27
Monoiso-amyl acid orthophosphate	59.4	1.4	30

In a further series of tests with the amyl acid phosphate it was found that reducing the amount of triethanolamine made clean-up more difficult. The presence of urea also aids clean-up although the standard formula containing 1.5% urea did almost as well as when the urea content was raised to 3.0%. Reduction of the organic amyl phosphate ingredient causes not only some increase in clean-up difficulty but also a serious loss of adhesive viscosity.

A mixture similar to the standard but containing clay had the following composition: 0.5 part of monodiamyl acid phosphate, 0.5 part of water, 0.2 part of NaOH plus 1.8 parts of water, 1.5 parts of industrial crystal urea, 0.5 part of technical triethanolamine, 94 parts of "N" sodium silicate and 1 part of Barden clay. This mixture had a viscosity of 45.5 Stormer seconds and a hot plate clean-up resistance of 2.1.

Example 6

A further illustration of the advantage of employing a silicate adhesive containing an organic amyl phosphate was carried out on a full plant scale. Two additive concentrates (concentrate #3 and concentrate #4) were pre-

pared ready for mixing with the regular plant silicate adhesive.

Concentrate #3 consisted of:

396 parts of urea
66 parts of triethanolamine
396 parts of water
5142 parts of "N" sodium silicate

This mixture was prepared by first heating the 396 parts of water to 150–160° F. The heat was then turned off and the 396 parts of urea were added to the water. The water was agitated during this solution period until the urea was completely dissolved. The solution had a temperature of about 80° F. Then the 66 parts of triethanolamine were added to the mixture with stirring until the liquid was entirely clean and uniform. This solution was then mixed with 5142 parts of "N" sodium silicate by adding the solution slowly in a small stream while vigorously stirring the "N" sodium silicate with a Lightnin mixer. Agitation was continued for 10 minutes after all of the mixture had been added. The final solution was allowed to stand for an hour until the foam had been entirely dissipated.

Another concentrate, concentrate #4, was prepared using:

90 parts of urea
162 parts of water
6 parts of flake caustic
30 parts of triethanolamine
42 parts of amyl acid phosphate
5670 parts of "N" sodium silicate

162 parts of water at ordinary temperature was placed in a mixing vessel and 42 parts of amyl acid phosphate was added without stirring. Then 6 parts of the flake caustic was added while the solution was agitated and agitation was continued until the solution became clear. Then 90 parts of the same crystal urea were added and the solution agitated until all was dissolved. Following this, 30 parts of the triethanolamine was added and thoroughly mixed in. This mixture was then added to 5670 parts of "N" sodium silicate in a larger mixing tank. The mixture was added slowly in a small stream to the sodium silicate in the vortex of the Lightnin mixer, and agitation was continued for 20 minutes after all of the solution had been added. The final mixture was then allowed to stand for about an hour until the foam had disappeared.

Concentrate #3 had a viscosity of 18.5 Stormer seconds while concentrate #4 had a viscosity of 40.6 Stormer seconds. When the plant adhesive was simulated using 88.3 parts of concentrate #3 and with 4.4 parts of starch and 7.3 parts of clay, the viscosity was 42.9 seconds and the clean-up force required was 2.0. With 83.2 parts of concentrate #4, 5.1 parts of water, 4.4 parts of starch and 7.3 parts of clay, the viscosity was 38.7 Stormer seconds and the clean-up force required was 1.8 pounds. These mixtures were designed so that the final viscosity would be in the range of a normal viscosity and the clean-up value below about 2 pounds. A standard plant adhesive was made up with 83.2 parts of "N" sodium silicate, 5.1 parts of water, 4.4 parts of starch and 7.3 parts of clay. This had a Stormer viscosity of 48.3 and a clean-up resistance of 9.5 pounds. In these tests the starch was a Hoosier pearl starch and the clay was Barden clay.

When run on the regular corrugating machine, the actual adhesive containing concentrate #4 exhibited no difficulty with odor, mixing or foaming or with corrugator operation or board quality. Clean-up around the single-facer and double-backer was definitely easier than with the regular adhesive, although the residue did not pop off without aid. The viscosity of a sample was 41.6 Stormer seconds and clean-up resistance was 0.2 lb.

When the plant adhesive containing concentrate #3 was used, some slight foam was noted. Corrugator operation and board quality were satisfactory and clean-up was easier than with regular adhesive. A sample had a viscosity of 30.3 seconds and the clean-up resistance was 2.3 pounds. This compares very favorably with the above figures of 48.3 seconds and 9.5 pounds clean-up resistance for the regular silicate-clay-starch adhesive.

These tests were run with B-flute. Kraft 42 pound liners and 26 pound bogus medium were combined at the corrugator speed of 290 to 300 f.p.m. The adhesives were pre-heated to a glue pan temperature of 117° F. with reduced steam used on the first few double-backer hot plates. The surface temperature of the first hot plate was 290° F. The adhesive made from concentrate #4 was somewhat less expensive in addition to giving less trouble with foaming and having a somewhat better self-release characteristic. While scraping was necessary on the hot plate, it required no real physical effort.

It has been determined that a truly self-releasing adhesive, that is, an adhesive which would pop off of the hot plate or be knocked loose by the movement of the liner board, must have a clean-up resistance no greater than 0.2 pound by our tests, preferably it should have a maximum resistance of 0.1 pound. We know of no so-called self-releasing silicate adhesive described in the prior art or used in practice which allows a clean-up resistance of as low as 0.1 pound on an uncoated or otherwise untreated hot plate surface. Truly self-releasing silicate adhesives have been obtained only with specially coated metal surfaces as described above.

The term "consisting essentially of" in the claims has been used to define the essential novel ingredients of the adhesive composition, but such words are not intended to infer that one could not incorporate into the claimed adhesive composition well known ancillary ingredients which would be obvious to those skilled in the art to which this invention pertains. The term "consisting essentially of" in the claims has been used to exclude components which would render the claims inoperative.

What is claimed is:

1. A novel adhesive composition having a low adherence to metal consisting essentially of:

(*a*) Aqueous sodium silicate,
(*b*) 0.25 to 2.0 wt. percent of an amyl ester of phosphoric acid, and
(*c*) At least one chemical compound selected from the group consisting of urea, sugar, triethanolamine and a condensation product of rosin and maleic anhydride and in the weight ranges of 1–5%, 1–5%, 0.1–2% and 0.1–2% respectively.

2. A novel adhesive according to claim 1 wherein the amyl ester of phosphoric acid is amyl acid phosphate.

3. A novel adhesive according to claim 1 wherein the amyl ester of phosphoric acid is monodiamyl phosphate.

4. A novel adhesive according to claim 1 wherein the amyl ester of phosphoric acid is monodi-iso-amyl acid orthophosphate.

5. A novel adhesive according to claim 1 wherein the amyl ester of phosphoric acid is mono-iso-amyl acid orthophosphate.

6. A novel adhesive composition having a low adherence to metal consisting essentially of:

(*a*) Aqueous sodium silicate,
(*b*) 0.25 to 2.0 wt. percent of an amyl ester of phosphoric acid, and
(*c*) Urea and triethanolamine in the weight ranges of 1–5% and 0.1–2% respectively.

7. A novel adhesive composition having a low adherence to metal consisting essentially of:

(*a*) Aqueous sodium silicate,
(*b*) 0.25 to 2.0 wt. percent of an amyl ester of phosphoric acid, and
(*c*) 1–5% urea and 0.1–2% of a condensation product of rosin and maleic anhydride.

8. A novel adhesive composition having a low adherence to metal consisting essentially of:

(*a*) Aqueous sodium silicate,
(*b*) 0.25 to 2.0 wt. percent of an amyl ester of phosphoric acid, and
(*c*) 1–5% sugar and 0.1–2% triethanolamine

9. A novel adhesive composition having a low adherence to metal consisting essentially of:

(*a*) Aqueous sodium silicate,
(*b*) 0.25 to 2.0 wt. percent of an amyl ester of phosphoric acid, and
(*c*) 1–5% sugar and 0.1–2% of a condensation product of rosin and maleic anhydride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,326,849	Fowler et al.	Aug. 17, 1943
2,671,747	Lander	Mar. 9, 1954
2,736,678	Olix	Feb. 28, 1956
2,772,996	Sams	Dec. 4, 1956
2,788,285	Lander	Apr. 9, 1957

OTHER REFERENCES

Ralph W. Kerr: Chemistry and Industry of Starch Academic, N.Y., 1950, page 304.