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NEWARK, NEW JERSEY

# NEWARK PLANT
# PIGMENT COLOR RESEARCH REPORT

## Progress Report

## AA-22-D MANGANOUS PYROPHOSPHATE

Period Covered JUNE, 1950 - JUNE, 1954 (PART TIME)

FILE: MR 210

DATE: 7/7/54

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

Progress Report

# AA-22-D MANGANOUS PYROPHOSPHATE

JUNE, 1950 - JUNE, 1954 (PART TIME)

CHARGE: 1101-11-182
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SUBMITTED BY: Julius Jackson J. JACKSON DATE SUBMITTED: 6/29/54

APPROVED BY: B. H. Perkins 7/2/54 B. H. PERKINS DATE ISSUED: 7/7/'54

DUP050069857

INTRODUCTION:

This report summarizes the status of work done on Manganous Pyrophosphate (AA-22-D) as a candidate pigment for the fortification of alkyd and lacquer paint systems.

For a general discussion of the broad objectives of this study, and the relationship to other pigments under study at the time, see KN-53-6. More recent work in this field has developed more promising candidates which are discussed in KN Reports 54-14, 18 and 19.

This pigment is also under study as a fortifier for unsupported organic polymers (see KN-54-15). Possible applications under investigation include -

A - Stabilization of polyvinyl chloride.
B - Decreased photo sensitivity of TiO2 delustered Nylon.

Despite the incompletion of this work, this report is being written at this time because of the writer's transfer to other work.

SUMMARY AND CONCLUSIONS:

1. This product has been studied extensively as a transparent film fortifier for alkyd systems. In its present form, (SW-1499) it is inferior in general durability characteristics versus other candidate film fortifiers such as -

| | |
|---|---|
| AA-33-D - Ferric Pyrophosphate | KN-54-18 |
| AA-34-D - Basic Nickel Carbonate | KN-54-19 |
| AA-36-D - Coprecipitated Cr/Fe Hydroxide | KN-54-18 |

in both alkyd and lacquer systems.

2. A coprecipitated 50 mol % Mn/50 mol % Fe pyrophosphate (NB 1446-53E) is showing excellent durability characteristics in alkyd (S-10399), being much superior to AA-22-D in durability at 9 months exposure, and more transparent than AA-33-D. If this product does not develop the typical bronze of AA-33-D (ferric pyrophosphate) between 9 and 12 months exposure, it could be the best of the transparent, colorless fortifiers so far developed in these studies.

3. AA-22-D is harder in texture than AA-33-D and this property would have to be improved if the product is to find any wide spread interest in dry form.

4. AA-22-D is the most transparent and colorless of all the candidates tested in alkyd and lacquer media. Despite this, semi-works and plant production have been possible without apparent contamination. Scrupulous attention to cleanliness of equipment is required in the manufacture of this type product.

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RECOMMENDATIONS FOR FUTURE WORK:

The following exposure series involving this pigment are under way and should be completed.

| SERIES | COMPOSITION | PRODUCTS TESTED | CONTROLS |
|---|---|---|---|
| 10343 | Al paints | AA-22-D - 1499 | Al paint - clear veh. |
| 10346 | Blue trim paint | AA-22-D - SD-1499 | A-6-D, GI-734-D, F-5-D, AA-33-D, AA-34-D, Clear veh. |
| 10399 | Clears - Metallics | 1446-53 | AA-33-D, AA-34-D, Clear vehicle. |
| 10430 | Vinyl paints | AA-22-D - 36877, 36754 | Clear vehicle. |
| 10432 | Vinyl sheeting | AA-22-D - 36877 | Clear vinyl |
| 10433 | Neoprene white wall stock | AA-22-D - 36754, 36877 | Neoprene white |

At this time, the use of AA-22-D as a fortifying pigment for alkyd or lacquer paint systems cannot be recommended. The fortification obtained is believed to be inadequate for commercialization of the product. As mentioned previously, other products, including the coprecipitated Mn/Fe pyrophosphate, seem to offer greater promise.

Applications in unsupported polymers (KN-54-15) may develop other possible uses for this material. Of particular interest at this time are the studies in polyvinyl chloride sheeting and paint systems.

Samples Under Evaluation by Various Groups.

| SAMPLE | TO WHOM | WHEN | PURPOSE |
|---|---|---|---|
| AA-22-D - 36877 | O.E.Ringwald(Pig.Dept.) | 6/11/54 | Paint studies |
| AA-22-D - 36877 | P. Lantos (Textile Fibers) | 6/1/54 | Nylon Fortification |
| AA-22-D - 36754 | L. Amborski(Film Dept.) | 4/27/54 | Mylar " |
| AA-22-D - 36877 | W. H. Madson | 3/18/54 | Polyvinyl Acetate |
| AA-22-D - 1499 36877 | D. Hulzlander(F&F Newburgh) | 1/6/54 | Polyvinyl chloride |
| AA-22-D - 1499 | W.Southard (Pig.Dept.) | 6/1/52 | White House Paints |

Numerous samples have been submitted to F&F for evaluation in paint systems (See DSN-53-3).

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REFERENCES:

DSN-53-3 AA-22-D General Studies.
54-7 Use of AA-22-D in unsupported Polymers.

KN- 53-6 Miscellaneous Inorganic Studies,
54-15 Use of AA-22-D in unsupported Polymers.

NB 1220, 1376, 1415, 1446, 1470

Monthly Summaries, Inorganic Laboratory, June, 1950 - June, 1954.

PATENT STATUS:

No investigation of the patentability of this compound as a film fortifier for alkyd or lacquer systems has been made.

The possibility of patentability of this compound for stabilization of vinyl systems has been discussed in KN-54-15.

A literature survey entitled "Chemistry of Manganous Pyrophosphate" has been written and a copy is attached hereto.

EXPERIMENTAL:

This product has been manufactured in the laboratory, semi-works and plant without difficulty. According to the reaction -

$$2MnSO_4 + Na_4P_2O_7 \rightarrow (Mn)_2P_2O_7)_x(Na_4P_2O_7)_y(H_2O)_z + 2Na_2SO_4$$

The composition of the material has been shown to vary with the $Mn^{+2}/P_2O_7^{-4}$ ratio present at the strike (see previously mentioned Literature Survey).

Typical analytical data are given in this memorandum.

The products obtained have been examined by X-ray techniques and are described as being amorphous. Electron microscopy indicates particle size is ±.2 to .3 microns.

Variable studies on this product are tabulated in Table I.

None of the variables studied, with the exception of the coprecipitation of Mn/Fe pyrophosphate 1415-53 under evaluation in S-10399, have shown a major improvement in the durability of this product in alkyd films.

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TABLE I

VARIABLE STUDIES ON AA-22-D

| SAMPLE | TESTED IN SERIES | VARIABLE STUDIES | RESULTS |
|---|---|---|---|
| 1220-63F | 10152 | Basic Process | Fair Durability, Low Gloss Retention |
| 1376-8 | 10152 | Dry form of basic process | " " " " " |
| 1376-20B | 10152 | Flushed Form of basic process | " " " " " |
| | 10153 | | |
| | 10164 | | |
| | 10167 | | |
| | 10168 | | |
| 1376-27 | | N-336 in place of CP $MnSO_4$ | ± color and durability. |
| 1376-31 | | Variation in $Mn^{-2}/P_2O_7^{-4}$ ratio | ± 10% variation had little effect on properties. |
| 1376-34) | | Evaluation of SW-1295 based on 1376-31D | ± = laboratory production. |
| SW-1295) | 10212 | | Fair Durability, Poor Gloss Retention - |
| | 10213 | | Blistering. |
| | 10214 | | |
| | 10219 | | |
| | 10247 | | |
| | 10262 | | |
| 1415-3 | 10268 | Variables on temp.-concentration reverse | Heat development improved gloss retentic |
| | 10325 | Strike - heat development | Properties of pigment in alkyd. |
| 1415-28 | | Effects of types of grading(Rod Milling) | Inconclusive - sample contaminated. |
| 1415-65 | 10326 | Effects of polyvinyl acetate treatment | Not beneficial to durability. |
| 1415-72 | 10326 | Effects of styrene treatment | Not beneficial to durability. |
| 1446-30 | 10387 | Heat development of various pH conditions | Little effect on durability. |
| 1446-36 | 10391 | Filming of AA-22-D with basic Ni Carbonate | Little benefit on " characteristics. |
| 1446-53 | 10399 | Tech. Mn vs CP Mn, heat development. | Coppt'd. Mn/Fe pyrophosphate. |
| | | Coprecipitation with Fe | Much superior to $Mn_2P_2O_7$ type |
| 1470-16 | | Variation in composition with $Mn^{+2}/P_2O_7^{-6}$ ratio | Composition changes with increased $P_2O_7^{-4}$ usage |
| 1470-18 | | " " " " | |
| 1470-27 | | Attempts to make soft textured AA-22-D for vinyl | Treatments not beneficial. |
| 1470-32 | | Pulp samples of AA-22-D for Nylon | Under evaluation. |
| 1470-41 | | Aqueous dispersions of AA-22-D for Nylon | Under evaluation. |

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Attempts at modification of durability by surface treatments or admixture with other agents in the paint films are described in KN-53-6. None of the treatments used was appreciably beneficial.

The effects of blending AA-22-D with various colored pigments is described in KN-53-6. The use of AA-33-D, AA-34-D, and AA-36-D gives better results insofar as durability is concerned versus Semi Works and plant production of AA-22-D in its present form (SW-1499).

The exposure history on this compound is tabulated in Table II.

Other Manganese Phosphates that have received study are -

$Mn_3(PO_4)_2$ 1220-63

$Mn_5(P_3O_{10})_2$ 1376-28, 47

MPH

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TABLE II

AA-22-D $Mn_2P_2O_7$ EXPOSURE PROGRAMS - STATUS AS OF 6/15/54

| SERIES | TYPE STUDY | VEHICLE | P/B | PVC | % Al | TYPE PANEL | EXPOSURE COMPL'D. | PIGMENTS TESTED | CONTROLS | CONCLUSIONS |
|---|---|---|---|---|---|---|---|---|---|---|
| 10152 | Single Pigment | Dulux | .16, .32 | 5% 10% | 0 | Steel | 12 Mon. | Dry & flushed* | Clear-Poly K. GI-734-D | Good film fortifier - not as good as Poly. K |
| 10153 | Blends BT-284 RT-428 RT-436 | Dulux | - | 2% 10% | 0,5 | " | 12 " | Dry & flushed* | 100% Toner | 20% extender/80% toner = to 100% toner. |
| 10164 | Blend GT-674 | Dulux | - | 10% | 10 | " | 12 " | Dry* | Guignet Green | Good tinctorial approximation - worse gloss reten |
| 10167 | Single Pigment | Dulux | - | 10% | various | Al | 12 " | Dry* | Clear + Al | Definite fortification |
| 10168 | Single Pigment Topcoats | Dulux | - | 10% | 0 | Al | 12 " | Dry* | Polymer K Clear | AA-22-D deficient in gloss retention vs Poly.K better than clear. |
| 10212 | Single Pigment | Dulux | .15 | - | 0 | Al | 12 " | Dry Semi-Works ** | Polymer K Clear GI-734-D | AA-22-D does not show appreciable film fortification. |
| 10213 | Single Pigment | Dulux | .15 | - | 1,5 | Al | 12 " | Dry Semi-Works ** | Polymer K Clear GI-734 | AA-22-D does not show appreciable film fortification |
| 10214 | Blend BT-284 YT-562 | Dulux | .11 | - | various | Al | 12 " | Dry Semi-Works ** | Polymer K Clear GI-734 | AA-22-D does not show appreciable film fortification. |
| 10219 | Blend BT-284 | Dulux | .16 .23 | - | 10 | Al | 12 " | Dry ** Semi-Works | BT-284 | Up to 50% AA-22-D ± = to 100% BT-284 |
| 10247 | Blend RT-525 RT-608 | Syn.26/ Res.881 | .17 | - | 5 | Al | 12 " | Post precipitated RT-525 on toner slurry RT-608 | | 50% extensions show decreased reactivity RT-608; decreased color change on baking; equal durability in masstones; inferior as metallic but Al/Toner ratio is two times control. |

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TABLE II Cont'd.

| SERIES | TYPE STUDY | VEHICLE | P/B | PVC | % Al | TYPE PANEL | EXPOSURE COMPL'D. | PIGMENTS TESTED | CONTROLS | CONCLUSIONS |
|---|---|---|---|---|---|---|---|---|---|---|
| 10262 | Single Pigment | Dulux | .25 | - | 0 | Al | 12 Mon. | Dry Semi-Works ** | Polymer K | AA-22-D inferior to Poly. K or $NiCO_3$ as film fortifier. Sli.fortification |
| 10270 | Single Pigment Blend F-4-P | Lacquer | .15 | - | 0 | Al | 9 Mon. | Pulp Semi-Works ** | F-4-P Clear | AA-22-D in pulp form inferior to F-4-P. Very sli.improvement over clear |
| 10273 | Single Pigment | Dulux | .35 | - | 5 | Al | 9 Mon. | Dry Semi-Works ** | Polymer K Clear | AA-22-D inferior to Poly. K; slight improvement over clear. |
| 10278 | Single Pigment | Various | .18 .61 | - | 0 | Wood | 12 Mon. | Dry and flushed** | Poly. K Clear GI-734 | Exposure incomplete. Sli. fortification; inferior to Poly.K or AA-34-D,AGI-734. |
| 10279 | Blend GT-674 | Syn.26/ Res.881 | - | 10 | 10 | Al | 12 Mon. | Dry Semi-Works ** | Guignet Green | Good tinctorial duplicati worse gloss retention. |
| 10284 | Single Pigment | Syn.26/ Res.881 | .35 | - | 0 | Al | 12 Mon. | Dry Semi-Works ** | AA-33-D Clear AA-34-D | Sli. film fortification; inferior to AA-33-D & AA-34-D. |
| 10286 | Single Pigment | Syn.26/ Res.881 | .35 | - | 10 | Al | 12 Mon. | Dry Semi-Works ** | AA-33-D A-34-D Clear | as 10284 |
| 10296 | Single Pigment | Syn.26/ Res.881 | .35 | - | 0 | Al | 6 Mon. | Dry Semi-Works ** | Clear | Exposure incomplete; no benefit at 6 Mos. |
| | | | | | | | | Effect of various anti-oxidants - buffers titanium organics. | | |
| 10303 | Blend | Lacquer | .15 | - | 5 | Al | 12 Mon. | Dry Semi-Works | Guignet Green | Crude + = GT-674. Guignet Green shows very slight advantage. |
| | | | | | | | | Evaluation crude green vs GT-674 in blends to simulate Guignet Green. | | |
| 10321 | 50% Blends RT-608 | Syn.26/ Res.881 | .17 | - | 5 | Al | 15 Mon. | various treatment, RT-608 | 100% RT-608 Clear | No advantage over toner + vehicle. |

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TABLE II Cont'd.

| SERIES | TYPE STUDY | VEHICLE | P/B | PVC | % Al | TYPE PANEL | EXPOSURE COMPL'D. | PIGMENTS TESTED | CONTROLS | CONCLUSIONS |
|---|---|---|---|---|---|---|---|---|---|---|
| 10322 | Single Pigment | Syn.26/ Res.881 | .35 | - | 10 | Al | 9 Mon. | various plant lots** | Clear | Fortification shown - gloss retention poor |
| 10325 | Single Pigment | Dulux | .35 | - | 5 | Al | 9 Mon. | Plant lot ** | AGI-73¼, Poly. K A-6-D, Clear | AA-22-D inferior, flushed GI-73¼; dry GI-73¼, A-6-D, AA-3¼-D in polish back and gloss retention. |
| 10326 | Single Pigment | Syn.26/ Res.881 | various | | 0 | Al | 12 Mon. | Dry S.W.** Effect of ultra violet screeners organic coatings | Clear A-6-D A-3¼-D | No appreciable improvement from agents; inferior to AA-3¼-D. |
| 10330 | Blend GT-674 | Syn.26/ Res.881 | .35 | - | 5 | Al | 12 Mon. | Heat developed Semi-Works** | Guignet Green | 12 Mon. durability very good ± = Guignet Green except for color retention. |
| 10340 | Single Pigment | Syn.26/ Res.881 | .25 | - | 5 | Al | 12 Mon. | Heat developed Semi-Works** | AA-33-D Clear | AA-33-D superior gloss retention. |
| 10341 | 50% Blend B-216 | Syn.26/ Res.881 | .25 | - | 5 | Al | 12 Mon. | Heat developed** | B-216-D A-33-D | AA-33-D shows superior gloss retention. |
| 10342 | 75% AA-22-D GT-674 YT-562 | Syn.26/ Res.881 | .25 | - | 5 | Al | 12 Mon. | Heat developed Semi-Works** | A-6-D A-3¼-D A-33-D GI-73¼ | AA-22-D inferior to AA-33-D, AA-3¼-D |
| 10343 | Single Pigme nt | Syn.55 | various | - | various | Al | 12 Mon. | Heat developed Semi-Works** | A-33-D Clear | Exposure incomplete. |
| 10344 | Blend RT-647-D | Syn.26/ Res.881 | .17 | - | 3 | Al | 12 Mon. | Heat developed** | RT-647 Clear A-33-D | A-22-D inferior to A-33-D extensions at 12 Mon. |
| 10346 | Blends BP-173 T102 | Syn.40 | - | various | 0 | Wood | 12 Mon. | Heat developed Semi-Works** | Clear A-6-D AGI-73¼-D A-33, A-3¼-D $CaCO_3$ | Exposure incomplete |

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TABLE II Cont'd.

| SERIES | TYPE STUDY | VEHICLE | P/B | PVC | % Al | TYPE PANEL | EXPOSURE COMPLT'D. | PIGMENTS TESTED | CONTROLS | CONCLUSIONS |
|---|---|---|---|---|---|---|---|---|---|---|
| 10386 | Single Pigment | Dulux various | - | - | 1.5 | Steel | 1 Mon. | Heat developed Semi-Works ** | Clear Guignet Green GI-734 | Blister resistance inferior to GI-734; approx. equal to Guignet Green |
| 10387 | Single Pigment | Syn.26/ Res.881 | various | - | 5 | Steel | 9 Mon. | Heat developed** anti-oxidants buffers | Clear | No appreciable improvement from treatments. |
| 10391 | Single Pigment | Syn.26/ Res.881 | .15 | - | 5 | Steel | 9 Mon. | $NiCO_3$ treatment; heat developed** Type 1 | Clear untreated control | No appreciable improvement from treatments |
| 10399 | Single Pigment | Syn.26/ Res.881 | .25 | - | 0,5 | Steel | - | Comparison type Mn salt. C.P. is technical | Clear A-33-D A-34-D | Exposure incomplete. Copptd. Mn/Fe Pyrophosphate very promising. |
| 10430 | Single Pigment | Vinyl | 3-10 | - | - | Steel | - | AA-22-D 36877 36754 | Clear | Exposure incomplete |
| 10432 | Single Pigment | Vinyl Sheeting | 3-5 | - | - | Steel | - | " " | Clear | Exposure incomplete. |
| 10433 | Single Pigment | Neoprene | 3-5 | - | - | Steel | - | " " | Clear | Exposure incomplete. |
| NEWPORT EXPOSURES | | | | | | | | | | |
| 11061 | Blend | Aroplaz 1271 | | - | - | Wood | 19 Mon. | AA-22-D SW-1295 | Yellow Paint | Checking |
| 11090 | Blend | | | - | - | Wood | 36 Mon. | AA-22-D SW-1295 | White Paint | Less chalking; more dust collection. |
| 11146 | Blend | | | - | - | Wood | 8 Mon. | AA-22-D 1499 | White Paint | Exposure incomplete |

* C.P. $MnSO_4$ used to prepare pigment.

** N-336 ($MnSO_4$-$(NH_4)_2SO_4$) used to prepare pigment.

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KN-54-17

c.c. J. N. Tully/A. Siegel
A. J. Stratton
B. H. Perkins
J. Jackson (2)

NEWARK, NEW JERSEY

MARCH 19, 1954.

MEMORANDUM FOR FILE:

CHEMISTRY OF MANGANOUS PYRO PHOSPHATE -

LITERATURE SURVEY.

The chemistry of the pyrophosphates of various metals has been studied by numerous workers. These experiments have shown that these "simple" compounds are, in fact, rather complex substances of indefinite composition.

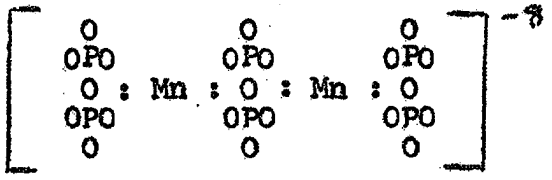
Vortmann (1) states that the reaction between manganous ions and pyrophosphate is as follows:

$$2\text{-}MnSO_4 + Na_4P_2O_7 \longrightarrow Mn_2P_2O_7\ 3H_2O$$

The compound is reported to contain 3 molecules of water if dried at 100°C, and 1 molecule of water if dried at 120°C. The reaction has also been studied by Pahl (2), who states that manganous pyrophosphate is sparingly soluble in excess pyrophosphate to form a compound $Mn_2P_2O_7 \cdot Na_4P_2O_7\ 9H_2O$. The nature of the compounds formed with excess of pyrophosphate is reported by Pahl to vary with conditions used.

$$Mn_2P_2O_7 + Na_4P_2O_7(\text{excess}) \xrightarrow[\text{heat}]{} 2\ Na_4P_2O_7 \cdot 3Mn_2P_2O_7\ 24H_2O$$

This solubility in excess pyrophosphate is apparently a function of pH, the simple $Mn_2P_2O_7$ being precipitated by the addition of acetic acid. This premise of complex pyrophosphate formation in excess pyrophosphate appears to be supported by Freed and Kasper (3), who describe the existence of $[Mn_2(P_2O_7)_3]^{-8}$ ions.



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Bassett (4) states that precipitation of metallic chlorides with equivalent weights of sodium pyrophosphate results in precipitation of amorphous solids which are quite persistent without becoming crystalline. These compounds, when dissolved by means of a weak acid such as sulfurous or acetic acid, followed by removal of this acid, give rise to crystalline hydrated pyrophosphates.

Manganous pyrophosphate is reported by Bassett to be very slightly soluble in excess of sodium pyrophosphate. The solid phase reported to be stable in this system is $Na_4P_2O_7 \cdot Mn_2P_2O_7\ 8H_2O$ (Pahl claimed $Na_4P_2O_7 \cdot Mn_2P_2O_2\ 9H_2O$).

$Mn_2P_2O_7$ is reported to be insoluble in excess of metal ions. Bassett gives the following compositions (Table I) for originally amorphous precipitates which have been allowed to become crystalline by prolonged shaking.

Inspection of Table I indicates that the stable compound formed when $Na_4P_2O_7$ is in excess is $Na_4P_2O_7 \cdot Mn_2P_2O_7\ 8H_2O$. Precipitation without large pyrophosphate excesses, followed by recrystallization in the presence of acid to remove excess $Na_4P_2O_7$, gives rise to compounds quite similar (in composition) to AA-22-D. Table II.

The conditions originally studied for precipitation of AA-22-D were based on the use of stoichiometric quantities of reactants at pH's below 7. These conditions would closely approximate certain examples of Bassett's wherein recrystallization was effected with sulfurous acid. A comparison of the analytical data show the composition of AA-22-D to fall into the expected range reported by Bassett. AA-22-D is reported to be largely amorphous by X-ray analysis with very slight evidences of crystallinity. The peaks which exist are accentuated by heat development of the product, but the product is not truly crystalline even after this treatment.

These studies indicate that for any patent purpose, AA-22-D cannot be considered a new composition of matter.

Julius Jackson

J. JACKSON
CHEMICAL DIVISION

JJ:MPH

REFERENCES:

(1) Vortmann Ber. 21 1104 1888.
(2) C.N. Pahl Ber. 6 1465 1873.
(3) Freed & Kasper J. A.C.S. 52 2632 1930.
(4) Bassett et al J. C.S. CXXXIX 1412 1936.

DUP050069868

## TABLE I

### LITERATURE DATE (BASSETT #4)

| Digestion Period | Mols $MnCl_2$ | Mols $Na_4P_2O_7$ | Drying Temp. | Yield Mol Mn | ANALYSIS FOUND % MnO | % $P_2O_7$ | % $Na_2O$ | % Loss on Ignition | % $SO_4$ | Calc. Ratio $\frac{Mn}{P_2O_5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| * | 1 | .473 | | | 38.03 | 37.92 | - | 23.96 | - | 2.01 |
| * | 1 | .536 | | | 41.70 | 44.47 | 1.03 | 12.83 | - | 1.88 |
| 12 days | 1 | 1 | | | 20.82 | 40.82 | 17.77 | 21.23 | - | 1.02 |
| 9 " | 1 | 1.5 | | | 20.88 | 40.90 | 17.72 | 21.9 | - | 1.02 |
| 9 " | 1 | 3 | | | 21.10 | 40.79 | 17.29 | 21.21 | - | 1.04 |
| $Na_4P_2O_7.Mn_2P_2O_7.8H_2O$ | | | | | 20.46 | 40.95 | 17.87 | 20.76 | - | - |

## TABLE II

### EFFECT OF $Mn/P_2O_5$ RATIO AT STRIKE ON COMPOSITION OF AA-22-D

| | Mol $Mn^{+2}$ | Mol $P_2O_7^{-4}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1470-16A | 1 | .35 | 140°F | 114 | 38.40 | 42.27 | .22 | 19.57 | - | 1.82 |
| 16B | 1 | .45 | " | 150 | 37.10 | 42.70 | .24 | 19.11 | - | 1.74 |
| 16C | 1 | .5 | " | 166 | 37.69 | 42.74 | .67 | 19.48 | - | 1.76 |
| SW-1295 | 1 | .5 | " | - | 37.10 | 41.70 | - | - | - | 1.78 |
| SW-1499 | 1 | .5 | " | - | 37.22 | 41.66 | 2.23 | 21.15 | .22 | 1.79 |
| Plt.36754 | 1 | .5 | 220°F | - | 36.85 | 43.61 | 4.72 | 16.13 | .52 | 1.69 |
| 1470-16D | 1 | .65 | 140°F | 192 | 35.15 | 46.48 | 6.15 | 15.43 | - | 1.52 |
| 16E | 1 | .75 | " | 200 | 33.94 | 48.53 | 9.17 | 12.96 | - | 1.40 |
| 16F | 1 | 1. | " | 206 | 34.56 | 48.40 | 14.13 | 9.81 | - | 1.43 |

*Amorphous precipitate dissolved in excess sulfurous acid and reprecipitated. (removes excess of sodium pyrophosphate).

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