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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Progress Report

AA-33-D - FERRIC PYROPHOSPHATE

Period Covered JUNE 1950 - JUNE 1954 (PART TIME)

FILE: MR 210

DATE: 7/8/54

Serial No. KN-54-18

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

Progress Report.

AA-33-D - FERRIC PYROPHOSPHATE

JUNE 1950 - JUNE 1954 (PART TIME)

CHARGE: 1101-11-182
1101-11-277

SUBMITTED BY: J. JACKSON Julius Jackson DATE SUBMITTED: 6/28/54

APPROVED BY: B. H. PERKINS B H Perkins 7/7/54 DATE ISSUED: 7/8/54

INTRODUCTION:

This report summarizes the status of work done on ferric pyrophosphate (AA-33-D) as a candidate pigment for the fortification of supported organic polymers and plastics such as alkyd and lacquer systems.

For a general discussion of the broad objectives of this study and its relationship to other pigments under study at the time, see KN-53-6.

This pigment is also under study as a flame retardent for cellulose acetate (see KN-54-16). Potential applications in unsupported plastics are discussed in KN-54-15.

Despite the incompletion of certain of these studies, this report is being written at this time because of the transfer of the writer to other work.

SUMMARY AND CONCLUSIONS:

1. This material is a good film fortifier for alkyd and lacquer systems. The major deficiency of the product in its present form (SW-1567, 1570) is a tendency to develop a heavy bronze in alkyd after approximately 9 months Florida 45°S exposure in alkyd, and lacquer paint systems. Color retention, polish back, and film integrity are all excellent.

2. A coprecipitated 50 mol % Mn/50 mol % Fe pyrophosphate (under evaluation in Series 10399 - KN-54-17) is showing excellent durability properties at 9 months exposure. Improvement of gloss retention in this product would be of definite interest.

3. AA-33-D (SW-1567) in its present form is inferior in gloss retention to other candidate film fortifiers such as AA-34-D (KN-54-19), or AA-36-D (KN-54-14), in alkyd systems. In other durability characteristics it is comparable or superior, and possesses the advantage of lower initial color and greater transparency versus these candidate pigments.

4. AA-33-D is superior to AA-34-D as a film fortifier for lacquer systems. Comparisons with AA-36-D seem to show an advantage for AA-36-D at 6 months exposure (S-10410).

5. The relatively low cost of AA-33-D and its soft texture make it a very attractive dry film fortifier candidate.

RECOMMENDATIONS FOR FUTURE WORK:

The following exposure programs are under way and should be completed.

SERIES	COMPOSITION	PRODUCTS TESTED	CONTROLS
10343	Metallics	SW-1567	Clear vehicle, AA-22-D
10346	Blue Trim Paint	SW-1570	Clear, A-6-D, GI-734, AA-22-D, AA-34-D, F-5-D.
10399	Clears-Metallics	SW-1567	Clear, AA-22-D, AA-34-D, Copptd. Mn/Fe pyrophosphate
10400	Metallics	SW-1567, 1570	Clear, GI-734-D
10402	Metallics	SW-1567	Clear, AA-34-D, F-4-P
10405	Clears, Metallics	SW-1567	Clear, AA-34-D, Polymer K
10407	Metallics	SW-1567, 1570	Clear, A-6-D, AA-34-D, AA-35-D, AA-36-D, Midas-Gold
10410	Metallics	SW-1567, 1570	Clear, A-6-D, AA-34-D, AA-35D AA-36-D.
10427	Clears-Metallics	1470-17, SW-1567	Clear, SW-1567
10429	Clears-Metallics	1470-22,23,24,29	Clear, SW-1567
10433	Neoprene Stock	SW-1567/1570	AA-22-D, Basic Aluminum Sulfate.

In addition to these studies current activities on the flame retardency of cellulose acetate and fortification in unsupported polymers should be completed. (See attached lists of samples submitted to various individuals).

Samples under evaluation by various groups:

Sample No.	Reference	Date	Purpose
	Unsupported Polymer Studies		
SW-1567	JJ - Amborski, Film Dept.	4/27/54	Mylar Fortification
	JJ - Cobbs, " "	4/13/54	" "
SW-1567	JJ - Bannerman, Textile)	4/27/54	Nylon "
SW-1567	JJ - Lantos Fibers)	6/1/54	Nylon "
SW-1567	R.H.Zabel - Luzena	4/6/54	Vinyl Flame Retardency
	" - "	4/8/54	
Various samples to Textile Fibers, Waynesboro			Cellulose Acetate Flame Retardency

DSN-54-8
KN-54-16

Samples submitted for Paint Evaluation

Sample No.	Reference	Date	Purpose
SW-1567 1570	G.W. - R.E.Pike, F&F	1/30/53	Paint application
1499	JJ - WFS - Newport	4/30/53	" "
1567	GW - R.G.Swanson, F&F	6/29/53	" "
1570	GW - " F&F	"	" "
1567/1570	JJ - S.C.Horning, F&F	11/24/53	" "

Attempts to modify the gloss retention characteristics of this pigment in alkyd systems are under evaluation in Exposure Series 1427, and 1429. Improvement of gloss retention in alkyd should make this product of considerable interest to the paint trade. Present durability characteristics of the pigment in lacquer systems are of interest to F&F. (P.T.S.R.#34 WFS, 6/4/54).

The potential uses in paint systems would involve such applications as -

1. Durable highly transparent clears.
2. Durable neutral grey metallic finishes when blended with aluminum.
3. Blending agent to give durable combinations with more highly colored and more expensive pigments.

The outcome of these studies should permit a decision as to the potential applications for this type product.

REFERENCES:

DSH-53-4	AA-33-D
DSH-54-7	Effects of transparent extenders on unsupported polymers.
DSH-54-8	Effect of AA-33-D on flammability of cellulose acetats.
KN-53-6	Speculative Inorganic Studies.
54-16	AA-33-D in Cellulose Acetate.
54-15	AA-33-D in Unsupported Polymers.
54-13,) 14,) 19)	Related studies on inorganic film fortifiers.

NB-1376, 1415, 1446, 1470.

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

PATENT STATUS:

No investigation of the patentability of the application of AA-33-D as a film fortifier for supported polymers (paints) or unsupported polymers has been made.

A patent proposal on the use of AA-33-D as a flame retardent, has been written (JJ - 6/23/54 - Metallic Pyrophosphates).

A survey of the literature concerning the chemistry of the ferric pyrophosphates has been made (JJ - Memo for File - 1/29/54) and a copy thereof is attached to this report. Patents on substances of related compositions that have been reviewed include - U.S.2,227,928, U.S.2,357,069.

The first experiment on AA-33-D is recorded in NB 1376-18 (JJ - dated 7/12/50). The product was revealed to others in the Inorganic Laboratory Monthly Summary of August 7, 1950, and in exposure program 10284 dated 12/28/51. No samples have been submitted outside the Company as of this date.

EXPERIMENTAL:

This product has been manufactured in the laboratory and in the semi-works without difficulty according to the following equation -

$$3Fe_2(SO_4)_3 + 3Na_4P_2O_7 \longrightarrow (Fe_4(P_2O_7)_3)_x(Na_4P_2O_7)_y(H_2O)_z + Na_2SO_4$$

The composition of the products obtained has been shown to vary with the $Fe^{+3}/P_2O_7^{-4}$ ratio used at the strike. (See summary in Memo by JJ - 1/29/54) "Chemistry of Ferric Pyrophosphate - Literature Review", which is attached to this report. Typical analytical data are given in this report.

The products obtained in the laboratory and semi-works have been examined by electron microscopy and X-ray techniques. The material is approximately .1 - .2 micron in size and amorphous to X-rays. (NB 1444-7 - File 210.2).

The specific gravities of the semi-works lots are 1567 - 2.07, 1570 - 2.04.

TABLE I

VARIABLE STUDIES ON AA-33-D

SAMPLE	TESTED IN EXP. SERIES	VARIABLES STUDIED	COMMENTS
1376-18D	10284, 6	Original process	good durability - poor gloss
1415-75	10340	pH, heat development Reverse strike	Heat development confers better gloss retention
1415-77	10340	Coprecipitated with $P_2O_7^{-4}/OH^-$	darker colors - ± = durability
1415-78	10340	Sources of Fe^{+3}, pH, volumes	approx. equal to $FeCl_3$ process.
1415-79	10341	B-216-D - AA-33-D	± = color retention, gloss retention, film integrity, less bronzing.
1415-81		RT-525-D - AA-33-D	greater transparency - poorer light-fastness.
1415-83	10344	RT-647-D - AA-33-D	better color stability.
1446-3		B-63-D - AA-33-D	better texture.
1446-4		F-5-D - AA-33-D	better texture.
1446-57	10400	Like 1415-78C	used as a pulp color.
	10402		No advantage over dry pigment
1470-12		$Fe^{+3}/P_2O_7^{-4}$ ratios	change in composition & yield
1470-14		" "	" " "
1470-15		Effect of Mg & Mn in copperas	darker colored products. result from higher impurities
1470-17	10427	$Fe^{+3}/P_2O_7^{-4}$ ratio	change in composition & yield
1470-22	10429	AA-33-D treated with Fe, Pb, Ca, Mn	flame retardency studies
1470-23	10429	AA-33-D treated with Hyponate, Arquad S, Naphthenic Acid, Silicone	" " "
1470-28		AA-33-D - effects of Al, Sb, Ti	" " "
1470-29		AA-33-D - use of $K_3H.P_2O_7$	under evaluation
1470-36		AA-33-D - use of Sb,Ti	flame retardency studies
1470-45		AA-33-D - use of Ti	" " "
1470-46		AA-33-D - use of Sb,Ti	" " "
S.W.1567	10340	Repeat 1415-78C type	good reproducibility and
1570	10340	" " "	duplication of lab. process
1737	10427	Study $Fe^{+3}/P_2O_7^{-4}$ ratio	under evaluation
1738	10427	" " "	" "
1739	10427	" " "	" "

TABLE II HORNING CONFERENCE - MAY 3, 1954

ALL PANELS FLORIDA EXPOSURE 45°S UNLESS OTHERWISE NOTED

AA-34-D - BASIC NICKEL CARBONATE

S-10262 - 12 Mos. Florida. Dulux 448/3078. 1:3 P/B = .25 Masstone.

#1 Flushed Polymer K, lot 10271.
#4 Dry $Ni(OH)_2$
#6 AA-34-D - 1376-78C. 1 Ni : 1 CO_3

S-10268 - 12 Mos. Florida. Dulux 448/3078. 1:3 P/B = .35 Masstone.

#1 Clear
#11 AA-34-D - 1415-9C. 1 Ni : 2 CO_3
#16 Polymer K - 10271

S-10278 -	12 Mos. Florida 45°S	18 Mos. N.J. 45°S	24 Mos. N.J. S.V.
Syntex 23/60 1:1	F-19-A Clear	J-19-B	J-19-C
	F-15-A AA-34-D	J-17-B	J-17-C
	F-16-A Dry $Ni(OH)_2$		
	F-18-A Blanc Fixe		
	F-17-A AA-34-D		

Dulux RC 448-3078				
1:2	F-39-A Clear	J-39-B		J-39-C
	F-38-A Poly K P/B = .16	J-38-B	AA-22-D .34 P/B	J-29-C
			Poly K .34 P/B	J-33-C
				J-38-C

Bakelite VF-1251	F-28-A Clear	J-28-B	J-28-C
	F-26-A $Al(OH)_3$ P/B = .20	J-26-B	J-26-C

S-10325 - 9 Mos. Florida. Dulux P/B = .35 5% Reynolds LN-37

#2 Polymer K - 10271
#9 Clear
#10 AA-34-D - 1415-61A 1:1 Ni/CO_3

S-10326 - 12 Mos. Florida. Syntex 26/Resimene 881 90/10 P/B = .35 Masstone.

#1 Clear
#2-3 AA-34-D 1415-61A 1:1 Ni/CO_3

AA-33-D $(Fe_4(P_2O_7)_{3X}(Na_4P_2O_7)_y(H_2O)_3)$

S-10284 6 Mos. + 12 Mos. Florida. Syntex 26/Resimene 881. 90/10 P/B = .35 Masstones.

#1 Clear
#3 Blanc Fixe
#7 AA-33-D - 1376-18D
#13 AA-34-D - 1415-9A 1:1 Ni/CO_3

S-10286 As above. 5% Reynolds LN-37

#1 Clear + Al
#3 Blanc Fixe
#7 AA-33-D
#13 AA-34-D

S-10340 12 Mos. Florida. Syntex 26/Resimene 881. 90/10 P/B = .25 5% Reynolds LN-37

#1 Clear
#11 SW-1567
#12 SW-1570
#19 Midas Gold 2344

S-10402 - 6 Mos. Florida. F-4-P. Two-roll lacquer. 4.5% Pigment
5% Albron #1570

#1 Clear
#4 AA-33-D - 1567 Dry
#6 AA-34-D - 1690 Dry
#8 F-4-P

S-10405 - 6 Mos. Florida. Syntex 26/Resimene 881.	P/B	% Al
#1 Clear	-	-
#2 AA-33-D - 1567	.25	-
#17 AA-33-D 1567-1570	.15	-
#15 AA-34-D 1690-1707	.35	-
#4 AA-34-D 1690	.25	-
#13 AA-34-D 1690-1707	.15	-
#19 Polymer K 50303	.15	-
#7 Clear + Al	-	-
#8 SW-1567	.25	5
#18 SW-1567-1570	.15	5
#16 AA-34-D 1690-1707	.35	5
#10 AA-34-D 1690	.25	5
#14 AA-34-D 1690-1707	.15	5
#20 Polymer K	.15	5

AA-36-D $85\ Cr^{+3}\ 15\ Fe^{+3}\ (OH)_3$

S-10342 - 12 Mos. Florida. Syntex 26/Resimene 881. 90/10 P/B .25
5% Reynolds LN-37

#2 AA-36-D
#3 A-6-D

USE OF EXTENDERS IN BLENDS

S-10342 (See above)

#24	Control	GT-674-D	P/B	= .06							
#5	"	"	"		+ AA-36-D	P/B	.20	=	Total	P/B	.26
#6	"	"	"		+ A-6-D	"	"	=	"	"	
#8	"	"	"		+ AA-34-D	"	"	=	"	"	
#9	"	"	"		+ M.G.2344	"	"	=	"	"	
#11	"	"	"		+ AA-33-D	"	"	=	"	"	
#12	"	"	"		+ Blanc Fixe	"	"	=	"	"	
#25	"	YT-562-D	P/B	= .06							
#14	"	"	"		+ AA-36-D	P/B	.20	=	Total	P/B	.26
#15	"	"	"		+ A-6-D	"	"	=	"	"	
#17	"	"	"		+ AA-34-D	"	"	=	"	"	
#18	"	"	"		+ M.G.2344	"	"	=	"	"	
#20	"	"	"		+ AA-33-D	"	"	=	"	"	
#21	"	"	"		+ Blanc Fixe	"	"	=	"	"	

S-10344 - 12 Mos. Florida - Syntex 26/Resimene 881								P/B	% Al	On Toner Basis
#5	RT-647							.17	3	
#6	"							.085	3	
#7	"							.0425	3	
#9	"	P/B	.0425	+ AA-33-D	P/B	.1275	=	.17	.75	
#11	"	P/B	.085	+ AA-33-D	P/B	.085	=	.17	1.50	Wet blend
#13	"	P/B	.085	+ AA-33-D	P/B	.085	=	.17	1.50	Dry blend

S-10346 - 12 Mos. Florida 45°S. Syntex 40

			PVC
#1	50/50	BP-173-D/R-610	10
#2		"	6
#3		"	4
#7		" + AA-33-D 6 PVC = Total	10
#8		" + Surfex 6 PVC = "	10
#10		" + AA-34-D 6 PVC = "	10

Other iron phosphates that have been examined include -

$Fe_3(PO_4)_2$ - NB 1376-18
$Fe_2P_2O_7$ - NB "
$FePO_4$ - NB "
$Fe_5(P_3O_{10})_3$ - NB 1470-24 (See Exposure Series 10429)

EXPOSURE PROGRAM STATUS:

A review of the status of transparent film fortifiers for paint systems was held with Dr. S. C. Horning of the F&F Department on 5/3/54 at Newark. Typical exposure panels, available at that time, covering AA-33-D and AA-34-D were shown. This information is summarized in the attached Table II and in an Office Trade Report of G. Wormald dated 5/3/54.

TABLE III

DATA ON REACTIVITY IN PAINT SYSTEMS

P/B = .15
42% Solids

Reading #4 Ford Cup in seconds.
Higher number - higher viscosity.

PIGMENT	SYSTEM	INITIAL	1 Week SHELF	1 Week 120°F	2 Weeks SHELF	2 Weeks 120°F	3 Weeks SHELF	3 Weeks 120°F	4 Weeks SHELF	4 Weeks 120°F	8 Weeks SHELF	8 Weeks 120°F
	Ford - Beckosol L 1307 - Resimene 881											
1567		19.5	21	23	22	25	22	27	22	30	22	
1570		19.5	21	23	21	25	22	27	23	30	23	
	Cook L-3314 - Uformite F-200-E											
1567		19.5	20	18	20	18	20	18	20	18	21	
1570		19.5	20	18	19	19	19	18	19	18	19	
	Dulux 448 - 3075 - 718											
1567		42	46	34	49	31	48	28	50	28	51	
1570		40	48	38	51	34	50	31	52	31	52	
	Syntex 26 - Resimene 881 *											
1567		47.5	60	120	71.5	170	90	237	103	-	131	
1570		46	60	109	71	155	85	230	100	-	122	
	Syntex 75 - Resimene 881 *											
1737		33	61	136	58	190	64	-	80	-	289(?)	
1738		31	60	132	54	166	60	-	75	-	102	
1739		31	58	124	55	168	57	-	73	-	106	

*Relatively higher reactivity for these systems has been noted with AA-34-D (KM-54-19) and F-13-D (KM-54-20).

TABLE IV AA-33-D $Fe_4(P_2O_7)_3$ EXPOSURE PROGRAMS STATUS 6/1/54

SERIES	TYPE STUDY	VEHICLE	P/B	PVC	% Al	TYPE PANEL	EXPOSURE COMPL'D.	PIGMENTS TESTED	CONTROLS	RESULTS
10284	Single Pigment	Syn.26/ Res.881	.35	-	0	Al	12 Mon.	1376-18-D	Clear AA-22-D AA-34-D	Product is very good film fortifier.
10286	"	"	.35	-	5	Al	12 Mon.	1376-18D	as above	as above
10340	"	"	.25	-	5	Al	12 Mon.	1415-75,77,78 SW-1567, 1570	Clear A-6-D GI-734-D AA-22-D Midas Gold	Best of dry products. Inferior to Midas-Gold in gloss retention only.
10341 with B-216-D	Blend	"	.25	-	2.5, 5	Al	12 Mon.	50% AA-33-D/ 50% B-216-D	B-216-D	Equal durability, less bronze.
10342 with GT-674-D YT-562-D	Blend	"	.25	-	5	Al	12 Mon.	75% AA-33-D/ 25% GT-674-D	A-6-D, AA-22-D AA-34-D Midas Gold	Inferior gloss retention vs AA-34-D, AA-36-D, Midas-Gold
								75% AA-33-D/ 25% YT-562-D	GI-734-D, GT-674-D, YT-562-D	
10343		Syn.55	various	-	various	Al	12 Mon.	AA-33-D, 1567	Clear AA-22-D	Insufficient exposure
10344 with RT-647-D	Blend	Syn.26/ Res.881	.17	-	3	Al	12 Mon.	50% AA-33-D/ 50% RT-647-D	RT-647-D AA-22-D	Extended products superior to unextended control at 12 months.
10346 with BP-173-D	Blend	Syn.40	-	10	-	Wood	12 Mon.	60% by vol. AA-33-D/ 40% BP-173-D	A-6-D, GI-734-D AA-22-D AA-34-D	AA-33-D inferior to AA-34-D - 12 Mos. Florida 45°S Surfex)
10386	Single Pigment	Dulux	-	-	1.5	Steel	1 Mon.	AA-33-D 1570 Imp.	AA-22-D GI-734-D X-1010	AA-33-D superior to AA-22-D, Imperial X-101(in blister resistance - inferior to AGI-734
10400	Single Pigment	Lacquer	-	-	5	Steel	9 Mon.	AA-33-D, 1567,1570 1446-57	F-4-P Guignet Grn. Clear, F-13-D GI-734-D	Inferior to Guignet Grn. & F-4-P - less colored, better than clear.

TABLE IV Cont'd.

SERIES	TYPE STUDY	VEHICLE	P/B	PVC	% Al	TYPE PANEL	EXPOSURE CONDITIONS	PITMENTS TESTED	CONTROLS	RESULTS
10402	Single Pigment	Lacquer	-	-	5	Steel	6 Mon.	AA-33-D 1446-57	Clear AA-34-D F-4-P	Better than AA-34-D and Clear. Inferior to F-4-P-but less colored
10405	Single Pigment	Syn.26/ Res.881	.15 .25		0,5	Steel	6 Mon.	AA-33-D 1567,1570	Clear AA-34-D Poly. K	Good fortification at 6 months.
10407	Single Pigment	Syn.75 Res.881	-	10	5, 7.5	Steel	6 Mon.	SW-1567 1570	A-6-D, AA-35-D, AA-36-D AA-34-D	Insufficient exposure
10410	Single Pigment	Lacquer	4.5 8.6	-	5	Steel	6 Mon.	SW-1567 1570	A-6-D, AA-34-D AA-35-D AA-36-D	AA-33-D better than AA-34-D,AA-35-D,AA-6-D. AA-33-D inferior to AA-36-D.
10427	Single Pigment	Syn.75/ Res.881	.15	-	5	Steel	-	1470 series SW-1737,8,9	SW-1567/ 1570 Clear	Insufficient exposure.
10429	Single Pigment	Syn.75/ Res.881	.20	-	5	Steel	-	1470-22,23, 24,29	SW-1567/ 1570 Clear	Insufficient exposure
10433	Single Pigment	Neoprene	.5/5	-	-	-	-		Neoprene	Insufficient exposure
NEWPORT SALES SERVICE SERIES - WHITE HOUSE PAINT										
S-11146						Wood	12 Mon.	SW-1567	T102 paints	8% bad chalking in house paint 12% "dirty"
F&F EXPOSURES - FLINT										
TX 5193	Single Pigment	Dulux	.10	-	?	Steel	8 Mon. & water soak	SW-1567 1570	GI-734-D Guignet Green	AA-33-D inferior* AGI-734-D, Guignet Grn. in blister resistance

*See Newark Series 10386. We have observed no blistering with this product in alkyd or lacquer.

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

NEWARK, NEW JERSEY

MEMORANDUM FOR FILE

JANUARY 29, 1954.

CHEMISTRY OF FERRIC PYROPHOSPHATE - LITERATURE REVIEW

This survey was undertaken to determine the possibility of claiming AA-33-D as a new composition of matter in a proposed patent.

The reactions between ferric ions and pyrophosphate ions have been studied quite comprehensively. Pahl (1) (2).

Pahl (1) Kung Svensk Vat Akad Handl Offers 30 7, 37 (1873)
(2) Berichte 6 1465 (1873)

States that ferric pyrophosphate is soluble in excess of pyrophosphate to yield solid solutions of varying composition:

$$Fe_4(P_2O_7)_3 + 5\ Na_4P_2O_7 \longrightarrow Fe_4(P_2O_7)_3 \cdot (Na_4P_2O_7)_5$$

$$Fe_4(P_2O_7)_3 + 2\ Na_4P_2O_7 \longrightarrow Fe_4(P_2O_7)_3 \cdot (Na_4P_2O_7)_2$$

More recently, Rodgers and Reynolds(3) have studied these

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(3) Rodgers and Reynolds J.A.C.S. 71 2081 (1949)

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reactions by conductimetric polagraphic, and potentiometric means. These workers have concluded that three inflections in the curves result when .1N metal solutions are titrated with pyrophosphate until precipitation occurs. Similar results were obtained by a reverse titration. These inflections occur at

	Metal/P_2O_7 Ratio	Complex ion
1st	.5	$[Fe(P_2O_7)_2]^{-5}$
2nd	.96	$[Fe\ P_2O_7]^{-1}$
3rd	1.33	$Fe_4(P_2O_7)_3$

Banerjee and Mitra (4) report $Fe_4(P_2O_7)_3$ is soluble in

(4) Banerjee and Mitra Science and Culture 16 530 (1951)
C.A. 46 8562 (1953)

excess sodium pyrophosphate and in the main substantiate the above findings. These workers also studied transport experiments and showed the presence of iron in the anode chamber (negatively charged particle), and absence of phosphorus in the cathode chamber (absence in positively charged particle). These studies substantiate the existence of the above mentioned ions.

Our studies of AA-33-D precipitation conditions reveal that yields and sodium content increase simultaneously with an increase in the $Na_4P_2O_7$ present at the time of precipitation.

AA-33-D Composition of Solids Dried at 140°F.

Reference	Ratio Mols Fe/P_2O_7	Yield Mo/Copperas	% Na
	$Fe_4(P_2O_7)_3 \cdot 9\ H_2O$ (Theory)	226.8	-
1470-12A	1:.64	240	.18
12B	1:.70	240	.44
12C	1:.714 (AA-33-D Std. Ratio)	246	.52
12D	1:.732	246	.88
12E	1:.77	248	1.30
14A	1:.79	256	1.00
14B	1:.827	256	1.46
14C	1:.865	265	1.76
14D	1:.902	298	2.30
16A	1:.64	230	
16B	1:.714	254	
16C	1:.77	258	
16D	1:.827	268	
16E	1:.907	276	

Variations are probably due to differences in moisture in various series.

These results may be explained on the assumption that a solid phase containing sodium pyrophosphate is being formed, and that this phase is not increasing in solubility with increased sodium content. The composition of the solid phase isolated at approximate stoicheometric ratios of ingredients cannot be quantitatively determined from existing data.

Typical analyses follow:

Code	Lot	% H_2O (Toluene)	Loss on Ignition	% Na	% Fe	% P_2O_5	% SO_4
AA-33-D	1567	22.0	29.8	1.9	20.63	40.86	.18
AA-33-D	1570	21.8	27.8	1.4	21.83	41.42	.35

The sodium content of these products is far too high to be explained as being present as sodium sulfate.

Indirect analysis calculations have been made on two bases:

(1) Solid phase is $Na_4P_2O_7$
$Fe_4(P_2O_7)_3$
H_2O

Calculation based on Fe and Na analysis.

(2) Solid phase is Na Fe P_2O_7
$Fe_4(P_2O_7)_3$
H_2O

Calculation based on Na and H_2O analysis.

Results of these calculations are tabulated below:

Premise (1)

	$Fe_4(P_2O_7)_3$	% $Na_4P_2O_7$	% H_2O Calc.	H_2O Toluene Distln. (Found)	Loss on Ignition
1567	68.9	5.24	25.86	22.0%	29.8
1570	72.8	3.56	23.64	21.8	27.8

Premise (2)

	% $Fe_4(P_2O_7)_3$	% $NaFeP_2O_7$	% H_2O	% Fe calc.	% P_2O_5 calc.	% Fe Found	% P_2O_5 Found
1567	58.1	20.0	22.0	21.9	44.4	20.63	40.86
1570	64.6	13.8	22.3	22.3	44.6	21.83	41.42

The latter calculations are not in as good agreement with the observed analysis, as the former.

These results lead to the conclusion that the product obtained at approximately stoicheometric ratios of Fe/P_2O_7 (see Table I) is essentially a solid solution of $Na_4P_2O_7.10\ H_2O$ in $Fe_4(P_2O_7)\ 9H_2O$. This, in the writer's opinion, can be predicted from a study of the literature and the composition is not novel. Some argument might be proposed as to why the compound contains sodium instead of being a normal ferric salt. Since these precipitates are amorphous, adsorption of sodium ions might explain their presence.

We have currently under study the question of composition of the solid phase versus utility of the pigment as a film fortifier. Based on earlier studies of AA-22-D, the writer does not believe that products containing higher sodium contents will be superior to the existing formulation; but tests are under way to determine if this is true.

In the writer's opinion, based on the information at hand, the basis of a patent for AA-33-D should be a "use" patent similar to the proposal on Polymer K.

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