NRL-54

REPORT NO. P-2141

FR-2141

DATE 6 August 1943

SUBJECT

The Replacement of Tung Oil in Navy Aeronautical Finishing Materials in Zinc Chromate Primer

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U. S. GOVERNMENT PRINTING OFFICE 16—21900

[redacted] SERIAL No. 24

14 August 1943 NRL Report No. P-2141

NAVY DEPARTMENT

First Report On

The Replacement of Tung Oil in Navy Aeronautical Finishing Materials - Zinc Chromate Primer

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Number of Pages: Text - 11 Tables - 5

Authorization: Bureau of Aeronautics letter dated 20 April 1942
Aer-E-2574-MVD F38(6-7) NP14,F38-2(12)

Date of Test: February to August 1943

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BuShips (3)

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ABSTRACT

This report describes the progress that has been made to date on the elimination of chinawood oil from Navy Aeronautical Specifications. Since the single item in which chinawood oil is most extensively used is zinc chromate primer, attention so far has been centered toward producing this primer with tung oil-free resins. The method of approach was to prepare resins having the characteristics of those occurring in zinc chromate primer which are free of chinawood oil. The first step in this process was to prepare an analog of the Bakelite BK-3962 dispersion resin based upon modified linseed oil. In order to provide a resin having properties more nearly resembling that of the standard, it was necessary to synthesize a considerable number from which the best were selected after numerous testing and evaluation experiments.

The second phase of this problem in so far as the primer is concerned concerns itself with the elimination of chinawood oil from the alkyd resin occuring in the standard formulation. A number of chinawood oil-free alkyd resins have been prepared and their evaluation is in process. Once a suitable resin of this type has been developed it will be incorporated into the primer formulation along with the proved outstanding dispersion type resin.

This report describes in detail the preparation of a number of resins of each type and also the evaluation of the dispersion type materials, that were synthesized. In addition, three outstanding dispersion resins were substituted for Bakelite BK-3962 in the standard formula for P-27-b primer and the resulting product evaluated against the standard as a control. By the simple expedient of substituting a modified linseed oil base dispersion resin for the tung oil containing standard two primers are described which appear almost as serviceable as the standard. This is believed to be an important contribution due to the fact that an adequately performing primer has been prepared in which a considerable amount of tung oil has been eliminated.

Future reports will deal with the continued progress of these experiments.

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INTRODUCTION

(a) Authorization

1. This study was authorized by Bureau of Aeronautics letter dated 20 April 1942 Aer-E-2574 NVS; F38(6-7); NP14; F38-2(12). A subsequent letter dated 9 July 1943 Aer-E-2577-MB/8-15-43, F38(6-7) requested specifically the report herewith submitted.

(b) Statement of the Problem

2. The object of this study was to investigate commercial substitutes for Tung Oil and to synthesize oils in the laboratory which may be used for the same purpose. The problem stated above was further confined for immediate work to the pursuit of a study of resins for use in P-27-b or AN-TT-P-656a zinc chromate primer which are free from Tung Oil.

(c) Known Facts Bearing on the Problem

3. Tung Oil is accepted to be the most nearly perfect drying oil known and any substitute which can be made by a practical process would almost certainly be inferior to it in performance as regards drying time, water resistance, alkali resistance, and weathering characteristics. The triply conjugated system of double bonds found in eleostearic acid has been shown to be responsible for these properties and no other oil contains such acids. Linseed oil contains linolenic acid which possesses three double bonds but it is present to the extent of only about 35% and the bonds are not conjugated. Hence, linseed oil is a slow drying oil and does not possess very good weathering characteristics or water resistance. In addition to these drawbacks the linolenic acid causes the film to yellow after a time.

4. The most promising alternate for Tung Oil is dehydrated castor oil which has been known for some time to possess excellent qualities as a drying oil, but it has been very difficult to obtain since almost our entire supply comes from Brazil and lack of shipping space has made this oil quite scarce. However, the situation has become much improved and according to latest reports there is ample castor oil on hand with a generous amount available because of the increased availability of shipping space.

5. The resins used in P-27-b or AN-TT-P-656a primer are typified by Rezyl 113 and Bakelite BK-3962, both of which utilize Tung Oil in their manufacture. The Rezyl 113 is an alkyd and the BK-3962 is a phenolic dispersion resin.

METHODS

Plan of Investigation

6. The plan of investigation falls into two catagories: the preparation of alkyds which do not contain Tung Oil, and phenolic dispersion resins which are also free of Tung Oil. A number of both types were prepared from

[redacted]

commercial oils and from synthetic oils prepared in the Laboratory. This study emphasizes dehydrated castor oil because it has shown more promise and can be obtained in sufficient quantities for immediate use.

7. Evaluation of these materials was accomplished by laboratory methods after which those showing the best performance were made into primers substituting them for the resin they were to replace. These primers were tested for all properties against the current specification requirements.

Materials

8. The dispersion resins prepared utilized a phenolic resin as an ingredient which in the majority of cases was Bakelite BR-254 except for three which were made with Bakelite BR-1329. The alkyd resins were made with phthalic anhydride and glycerol or pentaerythritol. Fatty acids were usually used in preparing the alkyd resins but oils themselves were heated with the phenolic resins. These for the most part were glyceryl esters although some were prepared from pentaerythritol.

9. The oils which were used for the dispersion resins are shown in Table 1.

TABLE I

Drying Oils Included in this Study

Name of Oil	Manufacturer	Type of Oil
Esskol	Spencer Kellogg	A treated linseed oil
Kellin	Spencer Kellogg	A treated linseed oil
Castung #403	Baker Castor Oil	A dehydrated castor oil
Castung #504	Baker Castor Oil	Bodied dehydrated castor oil
GF Oil	DuPont	Furylacrylic modified linseed oil
NRL #1	NRL	Pentaerythritol ester of dehydrated castor and furylacrylic acids
NRL #2	NRL	Pentaerythritol ester of dehydrated castor acids

10. These products were chosen because they are representative of the main types of drying oils offered as substitutes for Tung Oil. The Esskol and Kellin are typical treated linseed oils; the Castungs are typical dehydrated castor oils and the GF oil is an example of a synthetic oil using linseed as a base. The NRL oils illustrate the difference between a glycerol and pentaerythritol ester.

11. The fatty acids used in preparing the alkyd resins were obtained by saponification of the oils. The acids were used as follows:

a. Castung Special fatty acids
b. Castung #403 (alcoholized)
c. GF Oil (alcoholized)

Table II

Summary of Data on Properties of Dispersion Resins

Resin No.	Name of Oil	Wt. Oil	Oil Length	Wt. Phenolic	Wt. ZnO	% ZnO	Time of Rise	Beginning of String	Holding Time	Time of Heating after ZnO Addn
1	Tung	49.2 gms	10.5 gal.	100 gms	27.4 gms	18%	10 min	35 min	35 min	30 min
2	Tung	54	15	45	18	15	10	12	12	5
3	Esskol	54	15	45	18.4	15	10	40	42	5
4	Kellin	54	15	45	18.4	15	10	39	40	10
5	Castung 403	54	15	45	18.4	15	10	40	40	0
6	GF Oil	54	15	45	18	15	10	30	30	15
7	GF Oil	54	15	45	18	15	10	30	40	10
8	GF Oil	87.2	12	90.8	31.6	15	10	51	61	10
9	GF Oil	72.6	20	45.4	20.9	15	10	45	53	0
10	Castung 504	54	15	45	18.4	15	10	35	50	0
11	GF Oil	54	15	45*	18	15	10	25	25	0
12	GF Oil	87	12	90.8*	31.6	15	10	18	25	5
13	GF Oil	58	12	60*	21	15	10	31	30	0

Table II (con'd)

Resin No.	Name of Oil	Wt. Oil	Oil Length	Wt. Phenolic	Wt. ZnO	% ZnO	Time of Rise	Beginning of String	Holding Time	Time of Heating after ZnO Addn
14	NRL #I	54	15	45	18	15	10	45	50	5
15	NRL #II	54	15	45	18	15	16	34	44	0
16	NRL #III	54	15	45	18	15	10	25	30	5

*Bakelite BR-254 substituted by Bakelite BR-1329

Pentaerythritol was used rather than glycerol in most instances because of its well recognized superiority, and phthalic anhydride was the dibasic acid constituent in all cases.

METHODS OF PREPARATION OF MATERIALS

Preparation of Dispersion Resins

12. Dispersion resins are in reality short oil varnishes which are cooked almost to the point of gelling. The zinc oxide is then added to arrest the bodying action and prevent gelling. The resulting product after thinning to 50% solids is a very viscous mass which has very great stringing tendency. The following procedure describing the preparation of NRL Dispersion Resin No. 2 is a typical run of such a material. The variations on this method involve the use of different oils, phenolic resins, time of heating, and proportions of ingredients.

13. No. 2 NRL Dispersion Resin - This material was made with the idea of producing a resin as nearly like Bakelite BK-3962 as possible in performance and in appearance. This resin was of 15 gallon length and contained 15% zinc oxide.

Tung Oil	54 gm.
Bakelite BR-245	48 "
Zinc Oxide	18 "

The oil and resin were weighed into a 400 ml beaker and heated with a burner to 270° C in ten minutes and held at that temperature for twelve minutes at which time a good string formed. Then the zinc oxide was added and stirred into the mixture thoroughly. The heating was continued for five minutes more before the mixture was allowed to cool to 200° C and thinned with xylene to 50% solids.

14. The details of the preparation of the other resins of this type that were made are given in Appendix A. Table II summarizes the data onthe preparation of all these resins. Tung oil could only be heated to 270° without gelling, but all other oils were heated at 305° C.

Preparation of Alkyd resins

15. These resins consist of a mixed ester of a polybasic acid, such as phthalic anhydride and a polyhydric alcohol such as glycerol or pentraerythritol with unsaturated fatty acids as a polymerizable radical.

16. No. 3 Alkyd resin - The following experiment describes the preparation of a typical alkyd resin.

Baker's Castung Special fatty acids (1 mol)	280 gm.
Phthalic anhydride (1-1/2 mol)	222 "
Pentaerythritol (1 mol)	138 "

The above materials were placed in a liter three neck flask equipped with a

thermometer, a glycerine sealed mechanical stirrer and a moisture test receiver fitted with a reflux condenser. About 30 gm. of VMP naphtha was added to the material and the moisture test receiver was filled with the same solvent. In this way the water was carried over with the vapors of the VMP naphtha and condensed in the receiver while the solvent was returned to the reaction mixture. This provided a means of following the rate and extent of reaction. Table III shows a typical run for an alkyd resin. Details of the other resins prepared by this procedure are contained in Appendix B.

Table III

Reaction Rate for Alkyd Resin Preparation

Temperature	Time	Volume of Water (cc)
23° C	0 minutes	--
148° C	5	first drop
150° C	25	16.5
155° C	40	25.0
158° C	55	30.5
160° C	70	33.5
160° C	85	36.0
165° C	100	38.5
174° C	115	41.5
174° C	130	43.0
178° C	145	44.2
180° C	160	45.5
185° C	175	46.5
185° C	190	47.5
200° C	205	48.5
200° C	220	49.7
200° C	235	50.6
200° C	250	51.2
210° C	265	52.5
200° C	280	55.0
200° C	295	55.0

17. At the end of 295 minutes the viscosity was increasing rapidly and no further reaction was observable. The temperature was then allowed to drop to 150° C and the resin was thinned to 50% solids with xylene. Drier was added so that 0.3% lead and 0.03% cobalt were present. This resin dried overnight when flowed on a glass plate to yield a tough hard film.

Preparation of Acids

18. Fatty acids from drying oils - The general method for producing these acids was to dissolve four parts of potassium hydroxide in a minimum of water and add to thirty parts of alcohol. Then eight parts of the oil to be saponified were added with shaking. The clear orange solution was refluxed for four hours and poured into seventy parts of water acidified with an equivalent of sulfuric acid (2.2 parts). After stirring

thoroughly with a mechanical stirrer the acids were allowed to layer out and were decanted into a flask along with enough of the aqueous layer to carry over all of the acids. The flask was fitted with an outlet at the side so that the washing could be conveniently carried out. Thirty parts of water were added and the mixture boiled vigorously while CO_2 was passed through the mixture. Finally the acids were allowed to form a layer and the flask was tilted so that the aqueous layer could be drawn off from the outlet tube on which a stopcock was attached. This operation was repeated twice until the washings were no longer acid to alkacid test paper. Then the acids were transferred to an Erlenmeyer flask and dried with anhydrous sodium sulfate. The yield was about 95% in every case. These acids were stored in bottles filled with CO_2.

19. The above procedure was used to prepare the fatty acids from the following oils:

a. Castung Special 103 G-H
b. Castung 103
c. Kastolene
d. Roosenol #100

20. Furylacrylic acid - The furylacrylic acid used in these preparations was made by two methods. Both methods yielded material melting at 138 - 139° C with a molecular weight based on the acid number of 135 or 98% pure. The first method was reported by S. Rafagopalan; Proc. Indian Acad. Sci. 16A, 163 (1942), and the second method is found in Organic Syntheses, Vol. 20, page 55. It was found that light yellow material could be obtained by recrystallizing from water and decanting from the black tar which settles to the bottom and skins over on the top. Light yellow needles crystallize on cooling.

Preparation of Synthetic Drying Oils

21. Synthetic Oil-I - These oils differ from the parent glyceryl esters by being esters of pentaerythritol, which is a tetrahydric alcohol in which all hydroxyl groups are primary. The following materials were used:

Castung Special fatty acids	224 gm.
Pentaerythritol	27.2 "

These ingredients were placed in a three neck flask fitted with a mechanical stirrer, an inlet tube projecting below the surface, and a thermometer also immersed in the liquid. The temperature was raised to 150° C for two hours and then to 200° C for eight hours or until the acid number had dropped to 4. Carbon dioxide was continuously bubbled through the mixture as it was stirred. The final acid value was 3.6 and the iodine number was 129.8.

22. The details for the preparation of the other two oils of this series thus far prepared are given in Appendix C.

[redacted]

Preparation of Primers Containing Experimental Dispersion Resins

23. A gallon of stock primer was prepared by the formula given in Specification AN-TT-P-656a with the exception that the Bakelite BK-3962 was excluded. Aliquot portions of this stock were then taken and the proper amount of NRL dispersion resins to make up the deficiency was added. The primers so prepared were then tested against the standard according to the tests included in Specification AN-TT-P-656a.

METHODS OF TESTING

24. The dispersion resins were first thinned to a proper consistency for flowing on panels. Two glass and two aluminum panels were prepared in this manner of each of the dispersion resins and also Bakelite BK-3962 and the drying times noted. After drying for 24 hours the panels were tested for water and gasoline resistance by placing them in a pint can containing 200 cc of tap water or 40% aromatic gasoline. In this way the film was only half immersed in the liquid. Inspection of the films was made after 24 hours soaking. The results of these tests are summarized in Table IV. The tests were not all run simultaneously so that they cannot be grouped together.

Table IV

Comparative Tests on NRL Dispersion Resins

	Resin	No Drying Time Minutes	24 Hrs. Dry	Water 24 hrs. Glass	Water 24 hrs. Aluminum	Gasoline 24 hrs. Glass	Gasoline 24 hrs. Aluminum
A	1**	36	7*	6*	6*	1*	1*
	2	52	5	8	8	7	6
	3	33	4	5	5	5	3
	4	42	3	3	3	6	7
	5	36	8	7	7	8	8
	6	48	6	2	2	3	4
	7	20	2	1	1	4	5
	Bakelite BK-3962	35	1	4	4	2	2
B	8	50	4	2	2	2	1
	9	40	3	3	3	3	3
	10	30	2	4	4	4	4
	Bakelite BK-3962	30	1	1	1	1	2
C	11	60		7	7	5	7
	12	35		1	5	7	6
	13	70		2	6	3	5
	14	90		6	2	1	3
	15	70		5	1	2	2
	16	--		3	4	4	1
	Bakelite BK-3962	30		4	3	6	4

* These numbers illustrate the relative position of each resin with respect to all others tested in the same group.

**Several resins were made but were not tested because they served only to arrive at the optimum proportions of phenolic resin to oil and zinc oxide.

25. Group A dispersion resins No. 's 3, 6, and 7 were deemed worthy of incorporation into the P-27-b formula. The more promising resins of groups B and C will be incorporated into primers and described in a subsequent report. Therefore, a stock batch of this primer was prepared which contained no Bakelite BK-3962. The materials used were as follows:

Zinc Yellow	609.2 gm
Asbestine	107.6 "
Kopol #501	52.8 "
Rezyl #113 (60%)	585.2 "
Xylene	448.8 "
Maleic anhydride	4.4 "
Lead Naphthenate 12%	1.6 "
Cobalt Naphthenate 6%	.4 "

The weighed ingredients were thoroughly mixed and ground on the roller mill. One fourth of this stock was used with each of the dispersion resins and with Bakelite BK-3962 as control. Thus 90.7 gms of the dispersion resin was mixed into 494.5 gms of the stock material and run through the roller mill.

26. Tests according to Specification AN-TT-P-656a.

E-3. Physical Properties

E-3a. Appearance - The primers were all free of skins, lumps and grit and were easily mixed to a smooth homogeneous condition.

E-3b. Odor - Normal for the xylene used

E-3f. Skinning - #3 alone skinned after 48 hours in a container one fourth filled

E-3g. All samples were equal to the control with regard to the separation of pigment when thinned with three parts of toluene substitute conforming to Specification AN-T-8.

E-3h. Stability - Test samples on a full container which were stored for 96 hours at 49° C (120° F) showed varying ease of thinning but were not flocculated. The control thinned readily, #3 could not mix with the thinner to form a smooth mixture, #6 resembled the control except for a little more body, and #7 was intermediate because of the greater body than #6 but less than #3 and because of the difficulty of thinning.

E-4. Film Properties - Equal to the control

E-4a. Application Properties - Equal to the control

E-4a(1). Working Properties - All samples brushed and sprayed properly and leveled acceptably.

E-4b. Drying Time - All samples dried in air to handle within five minutes and were hard and tough in six hours.

E-4c. Surface Appearance - All samples after drying were free of streaks, blisters, silking and other irregularities of surface.

E-4d. Color - All experimental primers were somewhat green with #3 the deepest in hue.

E-4e. Flexibility - All samples formed films of sufficient flexibility since no cracking showed by the test specified in AN-TT-C-516.

E-4f. Metal Anchorage - Sprayed films after 18 hours air dry showed satisfactory anchorage in all cases.

E-4g. Coating Anchorage - A medium spray coat baked at 95 - 105° C (203-221° F) for four hours and recoated with L-12 lacquer showed satisfactory anchorage in all cases when the lacquer was air dried one hour and baked 16 hours at 95 - 105° C (203-221° C).

E-5a. Lacquer Resistance - No embrittlement, lifting, or other surface irregularities were shown in any case when a coat of lacquer was applied after the primer coat had dried for 10 minutes, 1,6,16, and 18 hours.

E-5b. Water Resistance - A flow out film, air dried, for 48 hours caused #3 to become much softer than the control while #6 and #7 remained harder than the control when immersed in distilled water for 24 hours. The adhesion of #3 was poorer than the control while #6 and #7 exhibited improvement.

E-5c. In gasoline the results were parallel to those in water except that the control was slightly harder than #6 and #7 and with #3 becoming very soft.

E-5c(1). An extension of the water and gasoline resistance test is a mixture of water and gasoline. This seems to be much more severe than either liquid alone. In this test the control became very soft and had no adhesion. In addition, it was covered with blisters which persisted 24 hours after removal. The #3 sample behaved the same as the control but the blistering which occurred disappeared within 24 hours after removal. The #6 sample behaved the same as the control in all respects while #7 remained harder retaining its adhesion and the blistering disappeared w ithin an hour after its removal from the water-gasoline mixture. However, the zinc chromate was leached from samples #6 and #7 to a greater extent that in the control.

E-5d. Weather Resistance (Durability) - Now on exposure and to be reported later.

Table V

Summary of Test Data on Experimental Primers

Requirement of AN-TT-P-656a Paragraph	Property	Bakelite BK-3962	#7	#6	#3
E-3	Physical properties	OK	OK	OK	OK
E-3a	Appearance	OK	OK	OK	OK
E-3b	Odor	OK	OK	OK	OK
E-3f	Skinning	OK	OK	OK	failed
E-3g	Settling	OK	OK	OK	OK
E-3h	Stability	OK	OK (-)	OK	failed
E-4	Film properties	OK	OK	OK	OK
E-4a	Application properties	OK	OK	OK	OK
E-4a(1)	Working properties	OK	OK	OK	OK
E-4b	Drying time	OK	OK	OK	OK
E-4c	Surface Appearance	OK	OK	OK	OK
E-4d	Color	OK	green	green	deepest green
E-4e	Flexibility	OK	OK	OK	OK
E-4f	Metal Anchorage	OK	OK	OK	OK
E-4g	Coating anchorage	OK	OK	OK	OK
E-5a	Lacquer resistance	OK	OK	OK	OK
E-5b	Water resistance	fair	good	good	failed
E-5c	Gasoline resistance	good	fair	fair	failed
E-5c(1)	Water and gasoline mixture resistance	fair	good	fair	fair

27. The foregoing data clearly indicate that it will be possible to replace Tung Oil in Bakelite BK-3962 the dispersion resin used in P-27-b primer. Of those incorporated in this formulation two appear to be satisfactory for this purpose, namely #6 and #7. Both these materials are the same except that the cooking procedure is slightly longer for #7 than for #6. The GF oil which is used to make these resins is a chemically modified linseed oil which is commercially available at the present time. Other dispersion resins have been prepared which show promise, but they have not been incorporated into primers as yet. However, in spite of the meager results reported herewith definite progress is evident.

28. The alkyd resins which have been described in another part of this report were prepared in order to determine whether or not the Tung Oil alkyd Rezyl 113 could be replaced. Since the properties which this type of resin imparts to the finished primer are much less tangible than are those contributed by the dispersion resin, the testing is more time-consuming and are therefore not yet completed. Subsequent reports will contain the results of these tests.

CONCLUSIONS

29. Three promising dispersion type resins free of tung oil have been prepared. Two of these function quite well when substituted for Bakelite BK-3962 in zinc chromate primer (P-27-b).

RECOMMENDATIONS

30. It is recommended that this study be continued to further eliminate chinawood oil from the alkyd resin constituent of the primer when a final recommendation may possible be made for a chinawood oil free product.

Appendix A

Altogether a total of 16 dispersion resins were prepared. The detailed data on this preparation is described in the following sections. The numbers listed in Table III in the main body of the report refer to the formulae numbered identically in Appendix A.

#1 Dispersion Resin

10 gal. oil length 18% zinc oxide

Tung Oil	49.2 gm
Glyceryl Oleate	5.5 "
Bakelite BR-254	100. "
Zinc Oxide	27.4 "

The oil and resin were heated in a 400 ml beaker to 270° C and held at that temperature for forty-five minutes. The zinc oxide was added at this point and the heating was continued for thirty minutes. When the temperature had fallen to 200° C xylene was added to bring the solids to 50%.

#2 Disperion Resin - Details of preparation given on page 4 of Report.

#3 Dispersion Resin

15 gal. oil length and 15% zinc oxide

Esskol	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18.4"

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes and held for forty minutes or until a string formed. Two minutes later the zinc oxide was stirred and five minutes later the mixture was cooled to about 200° C and thinned with xylene to 50% solids.

#4 Dispersion Resin

15 gal. oil length and 15% zinc oxide

Kellin	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18.4"

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes and held at that temperature for thirty-nine minutes or until a string formed. One minute later the zinc oxide was stirred in while heating was continued for nine minutes longer before it was cooled to about 200° C and thinned with xylene to 50% solids. This product was very viscous.

#5 Dispersion Resin

15 gal. oil length 15% zinc oxide

Castung #403	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18.4"

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes and held at that temperature for forty minutes at which time a string formed. At this point the zinc oxide was added and the heating was discontinued. When the mixture had cooled to about 200° C it was thinned to 50% solids with xylene. This product was very viscous.

#6 Dispersion Resin

15 gal. oil length and 15% zinc oxide

GF Oil	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18 "

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes, held at that temperature for thirty minutes or until a string formed. The zinc oxide was then stirred into the mixture. The heating was continued for fifteen minutes before allowing to cool to about 200° C and thinned to 50% solids with xylene. This product was smooth but darker and less viscous than Bakelite BK-3962.

#7 Dispersion Resin

15 gal. oil length and 15% zinc oxide

GF Oil	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18 "

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes and thirty minutes later showed a string. Ten minutes later the zinc oxide was stirred into the mixture, which was heated for an additional ten minutes before cooling to about 200° C and thinning with xylene to 50% solids. This material was more viscous than #10 but less so than Bakelite BK-3962.

#8 Dispersion Resin

12 gal. oil length and 15% zinc oxide

GF Oil	87.2 gm
Bakelite BR-254	90.8 "
Zinc Oxide	31.6 "

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The oil and resin were heated to 305° C in a 400 ml beaker over a period of ten minutes. After fifty one minutes the mixture began to show a string and at sixty one minutes, having almost gelled, the zinc oxide was added and stirred inthoroughly. The heating was continued for ten minutes longer before the mixture was allowed to cool to about 200° C and thinned to 50% solids with xylene. This was somewhat less viscous and resembled Bakelite BK-3962 very closely.

#9 Dispersion Resin

20 gal. oil length and 15% zinc oxide

GF Oil	72.6 gm
Bakelite BR-254	45.4 "
Zinc oxide	20.9 "

The oil and resin were heated together in a 400 ml beaker to 305° C in ten minutes. Forty-five minutes were required to produce a string and the zinc oxide was added eight minutes later when the material had almost gelled. A very thick product was obtained which was cooled to about 200° C and thinned to 50% solids with xylene thus producing a resin of thc same viscosity as Bakelite BK-3962, but rather grainy.

#10 Dispersion Resin

15 gal. oil length and 15% Zinc oxide

Castung 504	54 gm
Bakelite BR-254	45 "
Zinc oxide	18.4"

The oil and resin were heated to 305° C in a 400 ml beaker over a period of ten minutes. After thirty-five minutes at that temperature the mixture showed a string. Fifteen minutes later the zinc oxide was stirred in and when the temperature had dropped to about 200° C xylene was added so that the product contained 50% solids.

#11 Dispersion Resin

15 gal. oil length and 15% zinc oxide

GF Oil	54 gm
Bakelite BR-1329	45 "
Zinc oxide	18 "

The oil and resin were heated to 305° C in a 400 ml beaker over a period of ten minutes. Heating for an additional twenty-five minutes brought the material to a string and zinc oxide was added, stirred well as it cooled to about 200° C and finally thinned to 50% solids with xylene.

#12 Dispersion Resin

12 gal. oil length and 15% zinc oxide

GF Oil	87 gm
Bakelite BR-1329	90.8"
Zinc oxide	31.6"

The oil and resin were heated to 305° C in a 400 ml beaker over a period of ten minutes. A string began to show after eighteen minutes and after twenty-five minutes the zinc oxide was stirred in. The heating was discontinued five minutes after the zinc oxide addition and the xylene was added when the temperature had dropped to about 200° C to make it 50% solids.

#13 Dispersion Resin

12 gal. length and 15% zinc oxide

GF Oil	58 gm
Bakelite BR-1329	60 "
Zinc Oxide	21 "

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes. After thirty minutes the material began to show a string and the zinc oxide was stirred in. The mixture was heated for an additional five minutes before it was allowed to cool to about 200° C and thinned to 50% solids with xylene.

#14 Dispersion Resin

12 gal. length and 15% zinc oxide

NRL Synthetic Oil #1	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18 "

The oil and resin were heated to 305° C in a 400 ml beaker over a period of ten minutes. A string began to show after 45 minutes at this temperature and ten minutes later the zinc oxide was stirred in. After five minutes further heating the mixture was allowed to cool to about 200° C and thinned to 50% solids with xylene.

#15 Dispersion Resin

15 gal. oil length and 15% zinc oxide

NRL Synthetic Oil #II	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18 "

The oil and resin were heated to 305° C in a 400 ml beaker over a period of sixteen minutes. A string began to show after thirty four minutes of such heating, and the zinc oxide was added ten minutes later then the heating was discontinued. Then the temperature had dropped to about 200° C the mixture was thinned to 50% solids with xylene.

#16 Dispersion Resin

15 gal. oil length and 15% zinc oxide

Synthetic Oil #II	54 gm
Bakelite BR-254	45 "
Zinc Oxide	18 "

The oil and resin were heated in a 400 ml beaker to 305° C in ten minutes. After twenty-five minutes a string began to show and five minutes later the zinc oxide was added and the temperature maintained for five more minutes before the mixture was allowed to cool to about 200° C and thinned to 50% solids with xylene.

Appendix B

Five alkyd resins have thus far been prepared and the experimental details for their preparation are given below.

#1 Alkyd Resin

Castung 403 fatty acids	291.3 gm
Glycerol	61.3 "
Phthalic anhydride	148.0 "
Litharge	2.0 "

The Castung and glycerol were heated together with the litharge in a three neck flask at 200° C until alcoholysis was complete. This was shown by complete solubility of a sample in alcohol. The phthalic anhydride was then added and the reaction carried to completion using a moisture test receiver as described in the preceding preparation. The total reaction time was five hours at the end of which the temperature was lowered to 150° C and xylene was added to 50% solids. With driers added this gave a fast drying film, but was not tough enough.

#2 Alkyd Resin

Castung 103 fatty acids (2/3 mol)	170 gm
Furylacrylic acid (1/3 mol)	46 "
Phthalic anhydride (1/2 mol)	74 "
Pentaerythritol (1/2 mol)	68 "

Cooking time seven hours. Acid value 8.22. With driers this resin dried to a very tough film.

#3 Alkyd Resin - Details of preparation given on page of report.

#4 Alkyd Resin

Castung 103 fatty acids (5/14 mol)	100 gm
Linseed fatty acids (2/14 mol)	40 "
Phthalic anhydride (1/2 mol)	74 "
Pentaerythritol (1/2 mol)	69 "

Cooking time seven and one-half hours. The acid value was 1.89. With driers the resin dried well but was not a very tough film.

#5 Alkyd Resin

GF Oil (1/3 mol)	244.7 gm
Pentaerythritol (1/2 mol)	69 "
Litharge	1.2 "
Phthalic anhydride (1 mol)	148 "

Cooked for two hours at 200° C until alcoholysis was complete. Then the phthalic anhydride was added and the reaction mixture cooked for an additional two and one half hours. It was very viscous at this point, but the acid values was 45. After transferring to a beaker it was heated to 250° C while passing CO_2 through. It was then allowed to cool to 150° C and thinned. The final acid value thinned was 18.1. This was very viscous and with driers dried to touch in six minutes and became very hard overnight. The color was rather dark.

Appendix C

The drying oils described herein were prepared with what was believed to be the best combination of ingredients possible outside of tung oil itself. The pentaerythritol has four primary hydroxyl groups which makes for rapid and complete esterification resulting in a very high molecular weight compound. The furylacrylic acid was used because of the marked improvement rendered to linseed oil by, as for example, in the GF Oil of DuPont.

Synthetic Oil No. II

Castung Special fatty acids	187 gm.
Furylacrylic acid	46 "
Pentaerythritol	40 "

This reaction was run in a similar manner as the foregoing by holding at 150° C for one hour and at 200° C for five hours when the final acid value was 15.8 and the iodine number was 131.6.

Synthetic Oil No. III

Kastolene fatty acids	280 gm.
Pentaerythritol	40 "

This reaction was run in a similar manner as #I except that it was held at 170° C for two hours and 190° C for seven hours when the final acid value was 9.2 and the iodine number was 129.3.