國立交通大學研究所

化　學　組

油漆試驗報告

有

專　刊

化學類第三號

上　海

中華民國二十五年

研究所化學組油漆試驗報告

目　錄

研究所化學組本年度經過概況

徐名材

本校研究所化學組成立已逾六年。一方面從事分析檢驗工作,聊盡服務社會之天職。一方面研究油漆製造問題,冀達促進學術之志願。近一年來,繼續未停,用述概況,藉作報告。

(一)代辦事項　本年度接受外界委託事項,計有三十餘件;以煤,水爲較多,此外有礦砂,合金,硫酸,滑油石墨,汽油等項。茲列表於後,以見梗概:

號數	品物	委託人	樣品數目	樣品來源	報告單號數
1	煤	新通貿易公司	一	開平	一九二
2	錳粉	合衆電氣公司	三	湖南	一九三
3	河水	上海交通公司	一	黃浦江	一九四
4	汽油沉澱	航空委員會	一	未詳	一九五
5	煤	隴海鐵路局	四	井陘正豐煤礦	一九六
6	井水	南潯鐵路局	一	南昌南泵房	一九七
7	煤	正太鐵路局	一	山西太原西北煤礦	一九八
8	人造汽油	浙江建設廳	一	杭州民生廠	一九九
9	汽缸油	南潯鐵路局	二	美孚,德士古	二〇〇
10	石墨	范樂山先生	一	浙江	二〇一
11	煤	隴海鐵路局	一	山西鄉寧	二〇二
12	河水	新通貿易公司	一	無錫	二〇三
13	水泥	隴海鐵路局	一	西北實業公司	二〇四

14	井水	南潯鐵路局	一	南昌南泵房	二〇五
15	合金	中興煤礦公司	一	未詳	二〇六
16	煤	上海市公用局	二	未詳	二〇七
17	滑油	中華聯合工程會計事務所	三	亞細亞,孔士	二〇八
18	硫酸	交通部上海電話局	三	江蘇藥水廠	二〇九
19	鐵砂	張國瑞先生	一	浙江湖州	二一〇
20	軸油	正太鐵路局	三	未詳	二一一
21	煤	隴海鐵路局	一	宜陽煤礦	二一二
22	煤	隴海鐵路局	二	未詳	二一三
23	江水	江南鐵路公司	一	蕪湖江水	二一四
24	硫酸	交通部上海電話局	五	未詳	二一五
25	鉛礦	隴海鐵路局	一	未詳	二一六
26	河水	浦東電氣公司	二	黃浦江	二一七
27	鑄鋼	鐵道部購料委員會	二	未詳	二一八
28	煤	柏連坡煤礦公司	一	河南安陽	二一九
29	井水	隴海鐵路局	二	未詳	二二〇
30	煤	中華聯合工程會計事務所	一	安徽宣城	二二一
31	水	隴海鐵路局	二	老窰墟溝	二二二

(二)研究問題 本年度繼續進行研究問題,有(一)蓖麻子油製成乾性油之研究,(二)油溶性人造樹脂之研究,(三)桐油酸製合成油之研究,均爲油漆業重要問題。近年來各國人士注意研究者亦漸多結果多未公布,本組經數年試驗,已告一相當段落。本年度開始研究問題,有(一)羣青之試製,(二)青油作桐油代用品之研究,(三)蓖麻油製潤滑油之研究,(四)豆酪製水粉漆之研究,亦已得相當結果另有豆酪提煉一題,經化學系同人研究多年,茲亦擇要發表。此外學生論文工作,與油漆問題有關者,尙有生漆之研究,及什醇油中提煉溶劑之研究等。試驗結果,均詳研究報告中。

(三)添置設備 近來限於經費,對於試驗設備,未能儘量添置。

本年度新購者,計有石盤磨一具,三轅磨一具,以供少量試驗之用。另由化學系購硬度檢定器一具,價值千餘元,頗精密合用。目前急待需用,而無力購置者,有顯微照相器,以及乾率光度韌度檢驗器等件。

(四)工作人員　本組工作人員,多由化學系同人兼任。本年度担任分析工作者,爲謝惠袁積誠陳兆畦朱自立諸君;現陳君改就上海水泥廠職務,朱君改派他項工作,另聘萬葆德蔣孫穀二君繼任。油漆試驗方面,仍由沈慈輝君担任指導,分任研究者,有韋鏡權任通寶梁榮光諸君。

(五)試製儀器　油漆試驗器械,需費頗鉅,普通試驗室不能購備。茲擬先就最重要之比色計黏度計二項,計劃試製簡便儀器,以供製造及利用油漆者之採用,似亦本所應盡之責任。現在技術上困難問題,均已解決,下年度即可入手製造。

(六)審訂標準　油漆種類繁多,功用互異,品質高下,相去倍蓰,採用者每以選擇爲苦。吾國各鐵路及其他機關,對購買規範,尚未訂定,似有從速草擬之必要。本組擬參酌海外實用規程,考慮國內商業狀況,擬定一公允適用之標準,以供各界之參考,正在入手籌備中。

本組試驗結果,前已刊行報告兩期,茲復就年來研究所得,益以公餘撰述,彙集付梓。同人等課暇旁及,能力有限,設備多缺,補充無從,經年累月,愧鮮宏效。以視英國泰定頓油漆試驗所,成立不及十年,兩次擴充,已完成一偉大之研究機關者,望塵莫及,良深惶悚。第以油脂多吾國特產,塗漆尤建設必需,國計民生,不無關係,同人探求有年,不敢暇逸,勉効千慮一得之愚,冀獲銖積寸累之功。尚希海內明哲,予以贊助,時賜指教,俾作南針,尤同人所企禱也。

油漆試驗室下年度工作計劃

沈 慈 煇

下年度工作計劃,仍擬注重油漆問題,一方面就原有各題,繼續研求,一方面選急要工作,入手進行。玆將擬定計劃,撮述如下:

（一）油漆之抗鹼性能

油漆之用於鹼性物面,最易皂化,所以石灰或水泥之建築物塗漆之後,往往初則變色,日久漸漸剝落,永無耐久性能,如塗刷於其他物面者,此乃人所共見,亦無法制止之。然市售各種水泥漆,名稱雖異,實際上皆爲普通油漆之一種,而無耐久能力。本題擬根據各種學說試驗,並於物質上力求改良,使耐久不變,且於製造上合於經濟原則。

（二）防銹漆擴大試驗

本題已於二十三年擇要試驗,成績尙佳,所得結果,已見第二號報告。更擬擴大試驗,以收成效,乃因工作人員不敷分配,未得按照計劃,進行試驗。本學期仍應繼續工作,並將加製數份,送交鐵路當局試用,以覘試驗室與實地試驗結果之比較情形。

（三）從桐子餅提取桐油之試驗

桐油之用途漸廣,銷數亦增,是以供不應求,而致油價劇漲。但不知土法提油,終不能如機榨之純淨,且產量亦少。以每噸少提十分之一計算,則每年損失,幾及一二千萬元。按現在我國狀況,全國設立機製油廠,一時尙難實現,而每年幾千萬元之桐油,棄若糟粕,殊爲可惜。本題擬將桐餅設法提取餘油,以觀其成分及品質,所剩

殘渣,仍可供肥料之用,或有供飼料之價值,亦應逐一分別研究。

(四)蓖麻子油製成乾性油之研究

上年度曾將提煉之淨蓖麻子油,在普通氣壓蒸溜,得類似桐油之淡色乾性油,見第三號報告。以後試驗程序,仍按步進行,在蒸溜之過程中,擇定數點,取出油樣,加以詳細分析,以研究其化學組織之變化。

(五)羣青之試製

據上年在小電爐中試驗之結果,煆燒情形,及原料成分與色彩之相互關係,大致已可明瞭,見研究報告中。本年仍擬繼續原定方針,與半工業化之試驗,同時進行。前之試驗未週者,將加以補充,所得成品,均將詳細分析,並測驗其性能,以資比較。

(六)全國鐵路應用標準油漆及漆法之商榷

本題擬參考歐美各國鐵路用漆之標準,及現在各路採用油漆之種種困難問題,試行草擬各種標準油漆及漆法,使經濟而適合用途。

(七)油溶性人造樹脂之研究——曝露試驗

油溶性人造樹脂之研究,上年已將製造及性質兩部完成,唯其耐久性及施用後之變色與否,尚有待於探討。茲將製成之各種樹脂,用其純體及與亞麻子油配成之漆,製成樣片,於人工曝露機及天然曝露之下,分別進行曝露試驗,以完成對於人造油溶性樹脂之全部研究。

(八)蓖蔴子油經高壓加熱及接觸劑後性質變化之研究

此項研究,近年德法日等國,均分別舉行,各就其環境而從事研究,方法及原理均不相同。上年度進行人造油溶性樹脂之研究時,亦曾涉及此項研究,其結果頗可資為參考。故是項研究,殊饒興趣,并有實用上之價值。茲擬分為兩部進行:(一)利用國產磁土為接觸劑,(二)用高壓加熱,以覘其結果之優劣。

(九)氣相高壓裂餾棉子油之研究

此項研究,上年度即已計畫進行,因儀器之製造需時,未能早日進行。現儀器之主要部分,已裝置完畢,附件不日亦可裝配齊全,即可進行研究。

（十）蓖蔴油製潤滑油之研究

蓖麻油供飛機潤滑劑之用,由來已久,市上兼有礦物油攙和品。但平常蓖麻油與礦物油不相混合,須採特殊製煉方法方有效。上年度經作多次初步試驗,已獲相當結果,下年仍擬繼續研究。

PREPARATION OF OIL-SOLUBLE RESIN FROM POLYHYDRIC ALCOHOL AND POLYBASIC ACID. II.

JEN-CHUAN WEE (韋鏡權)

In the previous contribution on the same topic in the Report 1935, the preparation of an oil-soluble resin was reported. It is principally the introduction of fatty acid into the alkyd molecule to produce a resinous matter soluble in oil. It seems possible to prepare a great number of oil-soluble resins by varying the nature of oils, alcohols and fatty acids. Since the fatty acids and alcohols have their own special structures and properties, any one fatty acid radical or alcoholate radical in alkyd resin would impart to the resin some properties characteristic to itself. The combination of the peculiarities of both fatty acid and alcohol radicals in one single resin would cause much complexity in its properties and variation in its preparation. With a view of performing some scientific work along this direction, several resins are prepared and studied in detail.

As some fatty acids of the non-drying type have close relation in structure to those of drying type, it is possible to convert some non-drying fatty acid into drying type by proper treatments, that is, non-drying oil may be converted to drying oil and utilized in resin manufacture. The author carried out a series of experiments with this aim in view and prepared successfully one kind of such resins. This result might throw light on the field of research for new methods in resin manufacture by using non-drying oils.

In the present work, two polyhydric alcohols, glycerol and pentaerythrite, are used to prepare two series of resins. The resins containing glyceride residue are prepared by the methods, which, following the same principle as mentioned in the previous contribution, are the combinations of alcoholysis and esterification. The resins containing the pentaerythride residue are prepared by the other methods, which simply compose of the esterification of pentaerythrite in one stage or two stages, though similar to Scheiber's process (3) in general, but are different from it in detail.

Experimental

PREPARATION OF DIFFERENT TYPES OF RESINS

1. Pyro-casto-phthalo-glycero-resin

The raw materials used to prepare this resin are glycerine, phthalic anhydride, caustic soda and castor oil. Glycerine has to be dehydrated at 250-260°C. As the raw castor oil can not be used directly in this case, it is heated in carbon dioxide atmosphere on a sand-bath to 295-300°C with constant stirring by means of a continuous stream of carbon dioxide gas. The heating is continued for four hours. The castor oil undergoes transformation and decomposition, and a drying oil is obtained, which has higher iodine value and saponification value, but lower acetyl value than the raw castor oil. The oil thus obtained is called pyro-castor oil.

136 parts of dehydrated glycerine, 660 parts of pyro-castor oil and 2.4 parts of caustic soda are mixed in a vessel, which is fitted with a stirrer, an outlet for vapor and an inlet for leading in carbon dioxide gas to the bottom of the vessel. The caustic soda is dissolved in a little water or alcohol before use, in order to make it completely miscible with glycerine and pyro-castor oil. The mixture is stirred energetically under an atmosphere of carbon dioxide and heated in an oil-bath. The temperature is kept at 250-260°C. for one and half hours, and a slow current of carbon dioxide is passed in for stirring. The caustic soda acts both as a promoter for the dissolving of glycerine and pyro-castor oil, and as a catalyst for alcoholysis and esterification. Then, the mixture is allowed to cool down to room temperature under carbon dioxide atmosphere.

271 parts of phthalic anhydride is added and carbon dioxide atmosphere is restored. The temperature is raised gradually, and the efficient stirring is applied to make thorough mixing of molten phthalic anhydride and the pyro-casto-glyceride, because the former is lighter and may cause gelatinization at surface when the reaction takes place and no uniform product can be obtained. Oil-bath is preferred in this process in order to get even heating and at no time is its temperature allowed to go higher than 10°C. above reacting mixture. The reacting mixture is constantly stirred by a slow current of carbon dioxide which serves as well to carry out the water vapor. When the temperature of reacting mixture reaches 200°C., the heating is cautiously controlled to keep the temperature at 200-210°C. for two hours. Drying the last twenty minutes, the temperature may be preferrably raised to 210-220°C. to improve the quality of resin, and quicker stirring is necessarily applied

to prevent any possible local over heating. When the heating process reaches the final stage, the fire is removed and the resin thus obtained in quickly cooled by replacing the hot oil in bath with cold oil; this quick cooling is essentially, otherwise the resin would polymerize or have poorer solubility in oils and solvents. Stirring is continued until the temperature drops near 100°C. and the resin is rapidly taken out before it gets very viscous in the container at room temperature.

2. Tungo-phthalo-glycero-resin.

832 parts of Tung oil, 170 parts of glycerine and 4.2 parts of caustic soda are mixed under carbon dioxide. The air in the vessel must be displaced completely to prevent the oxidation of Tung oil during heating. The solid caustic soda has to be dissolved in small amount of alcohol before mixing. The reacting vessel used is the same as in the pyro-casto-phthalo-resin preparation. An evenly heated sand-bath may be used here. The mixture is vigorously stirred and quickly heated up to 250°C., and the temperature is kept at 250-260°C. for forty minutes. A current of carbon dioxide is continuously passed through the reacting mixture to carry off the vapor, and glycerine is refluxed down by a reflux condenser. Then, the temperature is rapidly raised to 280°C. while efficient stirring is maintained. The reacting mixture is kept at 280-290°C. for 10-15 minutes; longer heating would cause trouble in the next step in the process. The mixture is cooled immediately to room temperature under carbon dioxide, then transferred into another vessel, which is immersed in an oil-bath.

394 parts of phthalic anhydride is added to the cold Tungoglyceride obtained above. The air in vessel is displaced completely with carbon dioxide, then a slow current is maintained until the experiment is finished. The mixture is heated up rapidly; the temperature should rise to 190°C. in the least possible time, (within half an hour) even when large batch of material is handled. It is worth while to notice that the bath oil must not be heated over 210°C. in order to avoid any over heating of the reacting materials. When the temperature reaches about 100°C., the stirring is started with moderate speed in order to make thorough mixing of the ingredients. The temperature of the oil-bath and of the mixture is carefully controlled. A sudden rising or dropping in temperature may cause the reaction to be uncontrollable. When 190°C. is reached, the temperature is so adjusted as to raise to 200°C. gradually in a course of half an hour. In the next twenty minutes, it is steadily raised to 210°C. and finally to 215°C. The resin prepared is cooled and transferred in the same manner as in the case of pyro-casto-phthalo-glycero-resin.

3. Lino-phthalo-glycero-resin.

Raw linseed oil and glycerine are taken in the ratio of 778 to 167, and heated under an atmosphere of carbon dioxide above 250°C. for five and half hours. A slow current of carbon dioxide gas is passed in to stir the mixture and carry off any volatile matter. A great deal of albuminous matter in linseed oil is precipitated in the presence of glycerine. After heating has lasted two and half hours, the temperature is raised to 300°C. Finally the lino-glyceride is cooled under an atmosphere of carbon dioxide. The precipitate at bottom is removed to make the product clear.

31 parts of the clear lino-glyceride and 11 parts of phthalic anhydride are mixed in a vessel under carbon dioxide atmosphere. When the solid anhydride melts during heating, stirring is started. The temperature is kept at 240-250°C. for three and half hours. The water vapor resulting from the reaction condenses in the outlet and decreases in amount as the reaction goes to completion. The speed of the current of carbon dioxide is faster than that used in other similar preparations in order to prevent the darkening of the resin. The resin does not polymerize or gelatinize with ease, hence a longer time of heating is allowable. The resin is cooled with stirring under carbon dioxide just as in the case of other similar resins. It may be transferred when cooled on account of its high fluidity at room temperature.

4. Eleostearo-phthalo-pentaerythro-resin

The raw materials used are phthalic anhydride, α-eleostearic acid and pentaerythritol. The latter two compounds are prepared in the following manner. α-Eleostearic acid is prepared according to the procedure of Wang and Yang (4), with some modifications. 200 grams of high-grade Tung oil is refluxed with alcoholic potash consisting of 42 grams potassium dissolved in 400 ml. of 97% alcohol. The mixture is gently boiled on water bath for one hour. The clear hot solution is poured into 1500 ml. of 3% dilute sulfuric acid, and the mixture is stirred to make thorough acidification. On cooling, the cake of α-eleostearic acid above the aqueous layer is taken out, pulverized, washed, and then sucked dry. The crude α-eleostearic acid is purfied by recrystallization in 130 ml. of 97% alcohol, the alcohol being maintained at 35-40°C. and the acid is dissolved with stirring until saturation is reached. This solution is occasionally stirred to promote the crystallization when cooled. The crystalline α-eleostearic acid is filtered off, washed with small portions of alcohol, and then sucked dry. It is in the form of white shiny plates. The pure α-eleostearic acid is preserved under vacuum or under carbon dioxide in a dark and cold place, because it is readily oxidized in contact with air. It is advisable to store this acid in small portions in separate containers when it is prepared in large amount.

Pentaerythrite is prepared by a modification of the procedure described in Organic Synthesis (I). One liter of ice-cooled water is mixed with 71 grams of acetaldehyde and 560 grams of 40% formalin with stirring. Sixty grams of freshly hydrated pure lime is added to the solution in large portions with efficient stirring in order to bring up quickly the necessary alkalinity. The mixture is then heated in a water-bath to 60-65°C. with energetic stirring for two hours. When the suspended solids settle to the bottom, the clear lemon-yellow solution is decanted off and then filtered. A sufficient quantity of 50% sulfuric acid is added to precipitate the calcium in filtrate as calcium sulfate, but no excess of sulfuric acid should be present. The mixture is warmed, and the solid calcium sulfate is filtered off after settling. A saturated solution of oxalic acid is cautiously added to the hot filtrate, until a filtered sample no longer gives test for calcium salts. The liquor is concentrated under reduced pressure to 350 ml. and decolorized with active carbon; the filtrate is left over night. Crystals of pentaerythrite separated out on standing, this product is washed with cold alcohol, and recrystallized from water. The yield is about 114 grams.

377 parts of α-eleostearic acid, 154 parts of pentaerythrite and 226 parts of phthalic anhydride are mixed by grinding and placed in an autoclave. The air in the autoclave is displaced completely by carbon dioxide gas. The oil-bath is then heated up and the mixture is agitated gently. The slow current of carbon dioxide gas is temporarily stopped until the temperature of the mixture reaches 150°C., at which temperature all the solid melts and the frothing no longer occurs. The temperature of the reacting mixture is kept at 165-170°C. for one and one quarter hours, and then raised gradually to 180°C. in one and half hours. During the heating the temperature of the bath-oil has to be cautiously controlled to avoid any sudden rising; stirring is restlessly applied. The increase of viscosity, which is an indication of the stage of reaction, may be observed from the appearance and color of the foams on the surface. If the foam at the outer edge of the reacting mixture does not subside, but gradually increases in amount and turns deeper in color, heating should be immediately stopped even when the usual requisite time of heating has not reached. This resin is very viscous and sticky when cold. Therefore it must be transferred under carbon dioxide when hot. If air leaks into the autoclave, the yellow color of resin will change to brown or dark red.

5. Ricino-phthalo-pentaerythro-resin.

The ricinoleic acid is prepared from the ricinolein, which is isolated in pure state from castor oil. A mixture of 90% petroleum ether and 10% benzene is used instead of the Kransnodar benzine in Panjutin and Rapoport's method (2). Castor oil is extracted with a sufficient quantity of this mixture four times, and the solvent in castor oil is distilled off, the pure glyceride of ricinoleic acid being thus left behind. This glyceride is saponified with alcoholic potash, the alcohol is distilled off after two hours' boiling, much water is added and the mixture is distilled to drive out all the alcohol. The residual solution is acidified with hydrochloric acid and extracted with ether. The ethereal solution is washed and dehydrated. Pure ricinoleic acid is left in flask after distilling off ether.

475 parts of ricinoleic acid, 4.5 parts of litharge and 153 parts of pentaerythrite are mixed together; the litharge is finely ground and mixed with pentaerythrite, then ricinoleic acid is added. This mixture is heated under carbon dioxide on oil-bath, with constant stirring, the temperature being kept at 190-200°C. for one hour. Then the temperature is raised to 250-260°C. and maintained at this temperature for half an hour. The product is cooled down to room temperature under an atmosphere of carbon dioxide.

198 parts of phthalic anhydride is added to the ricinoleic pentaerythride and a carbon dioxide atmosphere is established. The mixture is heated to 190°C. with stirring, the temperature is kept at 190-200°C. for one hour and then raised to 200-210°C. in the course of half an hour. The resin is freed from the white suspension by dissolving it in toluene and distilling the solution after warming and filtration. Carbon dioxide is passed in to promote distillation and to prevent the resin from oxidation.

The properties of the resins prepared are shown in Table I.

Table I. Properties and Analysis of the Resins.

	Pyro-casto-phthalo-glycero-resin.	Tungo-phthalo-glycero-resin.	Lino-phthalo-glycero-resin.	Eleo-stearo-phthalo-pentaery-thro-resin.	Ricino-phthalo-pentaery-thro-resin.
Density	1.0764	1.1093	1.0566	1.1182	1.0873
Color (Gardner color standard)	11	12	15	11	12
Acid value	37.1	59.8	21.4	91.3	54.2
Saponification value	327.8	340.1	332.0	345.6	319.5
Ester value	290.7	280.4	310.6	254.3	265.2

Iodine value (Hanus)	89.5	99.0	105.1	166.0	65.7
Drying rate in room (hours)	6¼	46	21½	5/6	8 days
Drying rate in sun light (hours)	5	2	3	2/6	14
Gloss (Ingersoll glarimeter)	99.8	99.8	99.8	99.8	99.4-99.8

By studying Table I, we can note the following points:

(1). Among the phthalo-glycero-resins, Tungo-phthalo-glycero-resin has the highest density, largest acid value and smallest ester value. And, in the phthalo-pentaerythro-resins, the eleostearo-phthalo-pentaerythro-resin has the greater density, larger acid value and smaller ester value. These two relationships are similar, and may be attributed to the presence of Tung oil acid radical in molecule. Because the eleostearo-phthalo-pentaerythro-resin is prepared from pure α-eleostearic acid, the variations in density, acid value and ester value are more significant. Since the Tung oil acid in the Tungo-phthalo-glycero-resin consists only partly of α-eleostearic acid, the variations in density, acid value and ester value from other resins are smaller than those of eleostearo-phthalo-pentaerythro-resins.

(2). Among the phthalo-glycero-resins, lino-phthalo-glycero-resin has the smallest density, least acid value and highest ester value. These characteristics are just opposite to those of the Tungo-phthalo-glycero-resin. The corresponding figures of pyro-casto-phthalo-glycero-resin have intermediate values, though approaching those of lino-phthalo-glycero-resin.

(3). The difference between the drying rate of pyro-casto-phthalo-glycero-resin in a room (diffused light) and its drying rate in direct sunlight is comparatively slight, while the corresponding difference for the other resin amounts to a considerable value. This shows that the fatty acid in pyro-casto-phthalo-glycero-resin has special characteristics and the cause of drying of such resin is somewhat different from others. The pyro-castor oil has been subjected to corresponding tests, and the results is similar to those of the pyro-casto-glycero-resin.

(4). From these results, the conclusion may be drawn that the nature of the fatty acid radical and alcoholate residue contributes to the corresponding resins certain characteristic properties.

Miscibility of Resins with Oils.

Lino-phthalo-glycero-resin is miscible with all oils and can be blended in any proportion. The other resins, when mixed with oil and heated at the proper temperature, produce the blendings which can stand dilution with two to four times of petroleum solvent. It is noticeable that the resins may be very easily blended with the oils containing the same fatty acid radical. The tolerance to dilution of the resins prepared are shown in Table II.

Table II Tolerance to Dilution of the Resins.

	Pyro-casto-phthalo-glycero-resin.	Tungo-phthalo-glycero-resin.	Lino-phthalo-glycero-resin.	Eleo-stearo-phthalo-pentaery-thro-resin.	Ricino-phthalo-pentaery-thro-resin.
Alcohol	0.4	0.64	0.27	2.2	1.5
Ether	2.5	1.45	∞	10	∞
Mineral turpentine	4.5	0.8	"	0.5	0.7
Petroleum ether	0.5	0	"	0.25	0.33
Vegetable turpentine	∞	16.5	"	6	15
Toluene	34	3.2	"	3.3	30

From Table II we can see:

(1) All the resins are very soluble in vegetable turpentine, but less so in toluene.

(2) Phthalo-pentaerythro-resin is miscible with both ether and alcohol, and in this respect is quite distinct from phthalo-glycero-resin.

(3) Pyro-casto-phthalo-glycero-resin is similar to Tungo-phthalo-glycero-resin and different from lino-phthalo-glycero-resin with regard to its solubility in ether, petroleum ether, toluene and mineral turpentine.

(4) Lino-phthalo-glycero-resin is a peculiar member among the resins prepared in showing extremely low solubility in alcohol and extremely high solubility in other solvents.

Summary

(1) Three oil-soluble resins containing glyceride residue are prepared by alcoholysis of pyro-castor oil, Tung oil, and linseed oil respectively, with glycerine at 250-260C. with or without catalyst, and by esterification of the product with phthalic anhydride at different temperatures in the range of 190-250°C.

(2) Two oil-soluble resins containing pentaerythride residue are prepared respectively by (a) esterification of pentaerythrite with mix-

ture of α-eleostearic acid and phthalic anhydride, and by (b) esterification of pentaerythrite in two stages with ricinoleic acid at 190-250°C, and with phthalic anhydride at 200-210°C.

(3) The constants of the resins are given in the order of casto-phthalo-glycero-resin, Tungo-phthalo-glycero-resin, lino-phthalo-glycero-resin, eleostearo-phthalo-pentaerythro-resin and ricino-phthalo-pentaerythro-resin; the iodine value: 89.5, 99.0, 105.1, 166.0, and 65.7; the color in Gardner's color standard: 11, 12, 15, 11, and 12; the drying rate in room: 6¼, 46, 21½ 5/6 hours and 8 days; the drying rate in sun light: 5, 2, 3, 2/6 and 14 hours. The nature of the fatty acid radical and alcoholate residue contributes to the corresponding resin certain characteristic properties.

(4) Lino-phthalo-glycero-resin is highly soluble in all solvents (except alcohol) and miscible with oils. Pyro-casto-phthalo-glycero-resin is similar to Tungo-phthalo-glycero-resin in tolerance to dilution. Ricino-phthalo-pentaerythro-resin and eleostearo-phthalo-pentaerythro-resin are compatible with both alcohol and ether, but their solubilities in other solvents are poorer than those of other resins.

(5) Oil-soluble and drying resin may be prepared from castor oil by proper treatment. This opens up a new field of research for methods of utilizing non-drying oils.

Acknowledgement

The writer would like to offer his sincere thanks to Prof. M. T. Hsu (徐名材), Chief of Division of Chemistry of the Research Institute of Chiao-Tung University, for his encouragement of this research work; to Prof. T. H. Shen (沈慈輝), Chief of Paint Laboratory, for his suggestions and advices; and to Mr. T. Y. Tang (唐藎源), Chief of Chemical Laboratory of Commercial Press, for his courtesy in granting the use of glarimeter.

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提要

自多元醇與多價酸製成油漆性樹脂之（二）

1. 於 250－260°C 之溫度,用接觸劑,或不用之,使甘油與桐油,或亞麻仁油,或曾經特別製煉之蓖麻油,分別起醇化作用。再將其產物與二甲苯酸,於190－250°C 之間之溫度,分別酯化,則得含甘油根之油溶性樹脂,共計三種。

2. 又用戊四醇製成油溶性樹脂二種,其法各別:（一）使戊四醇與桐油酸及二甲苯酸之混合物酯化;（二）使戊四醇與蓖麻油酸,於 190－250°C 之間之溫度酯化,又於 200－210°C 與二甲苯酸酯化。

3. 各種油溶性樹脂之性質,擇要選列於下:

	碘價	顏色	室中變乾時限	日中變乾時限
煉蓖麻二甲苯甘油樹脂	89.5	11	6¼時	5時
桐油二甲苯甘油樹脂	99.0	12	46時	2時
亞麻二甲苯甘油樹脂	105.1	15	21½時	3時
桐油二甲苯戊四醇樹脂	166.0	11	5/6時	2/6時
蓖麻二甲苯戊四醇樹脂	65.7	12	8日	14時

樹脂中所含之脂肪酸根及醇基,對於樹脂,能賦予種種特異之性質。

4. "亞麻二甲苯甘油樹脂",能與油類溶和,各種溶劑除酒精外,均能溶之。"煉蓖麻二甲苯甘油樹脂",對於溶劑之性質,則與"桐油二甲苯甘油樹脂"相近似。至於"桐油二甲苯戊四醇樹脂"與"蓖麻二甲苯戊四醇樹脂",則在醇與醚中,均能溶和,但對於其他溶劑,則不若各種甘油樹脂之易溶。

5. 蓖麻油經合宜之煉製後,可用以製成有乾性之油溶性樹脂,此於利用非乾性油於製造樹脂之研究,實開一新徑。

STILLINGIA OIL AS A SUBSTITUTE FOR TUNG OIL

T. H. SHEN (沈慈輝)

The ever increasing demand for tung oil has made the price soared tremendously in both Chinese and foreign markets during the past year. The actual present price of tung oil has practically tripled the price two years ago; yet judging from the present market condition, it is still in the upward trend so long there is no immediate method to increase the production. Inasmuch as the price of tung oil remains at such a high level, naturally the substitution with some other oils is being seriously considered, but it is not very hopeful in the immediate future for some reason or other, though many researches have been made along that line. *Oiticica oil has been suggested as a substitute, but results of numerous experiments do not show any sign of encouragement. The blending of this oil to tung oil for making varnishes merely degenerates the standard quality of products. Synthesis of drying oils from non-drying oils has met with some success but there could be nothing so quick in drying and so impervious to water like tung oil. Partial substitution of this synthetic oil in paint and varnish is not possible to produce the exact same quality as those made from tung oil. Moreover the price of synthetic oil is another factor which hampers its wide use in replacing tung oil.

Out of all difficulties there has been one oil which is also indignant to China and possesses drying properties. It is called stillingia oil obtained from seeds of Stillingia Sebifia or Sapium Sebiferum, Roxb. belonging to the family of Euphobiceae. It is a deciduous tree growing wild in all provinces along the Yangtse Valley and flourishes best in low swamp lands. In July it flowers and late in fall it bears fruits abundantly in clusters. By grafting seedlings of two years old which are about 2-3 ft high, each will bear fruit amounting to 20 pounds by the end of third year and 50 pounds by 5th year. The seeds are enveloped in a black husk usually three in number. The outside waxy covering of the seed attached to the shell of the kernel is called mesocarp from which vegetable tallow can be obtained. The inside kernel, when pressed, gives an oil of straw yellow color. As to the com-

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*P & V Production Manager p32, Nov. 1935.
H. F. D Brookes p36, Feb. 1936.

position of the seed reference may be made to J. & Proc. of the China Soc. of Chem. Ind. II pt 1, 60 (1924). The crude oil is usually contaminated with some vegetable tallow in the process of manufacturing which is inavoidable by the native method. It is imperative to remove this tallow in order to improve the quality of oil. Refining process has been studied by several experimenters and the *best method worked out in this laboratory is to extract the solid oil at an extremely low temperature with excessive dilution by acetone.

The analytical data shown in Lewkowitch and other places are as follows:

	Sp. gr.	Sap. val.	Iod. val.	Observer
1	.9458	203.8	154.6	Hebein
2	.9432	210.4	160.6	Tortelli & Buggeri
3	.9395	—	60.7	Nash
4	.9390	203.2	145.1	Laucks
5	.9392	205.6	165.	Shen

According to Lewkowitch the most characteristic property of this oil is its optical rotation viz. -6° 45′ in a 200 mm. tube in a Laurent polarimeter, corresponding to -29.9 Saccharimeter degrees.

Experiment

I. DRYING PROPERTIES OF STILLINGIA OIL

Stillingia oil, when not treated, is very thin and not suitable for use as paint and varnish oil. For instance when it is painted on a smooth surface, it "runs" or crawls in streaks or droplets like perilla oil due to its high surface tension. Thus a paint made of raw stillingia oil is very thin and not comparable with raw linseed oil paint, as the paint does not work very well under the brush. Nevertheless, the valuable property of this oil is its rate of drying and the character of film produced when properly treated. It is observed when a small amount of drier is incorporated into the boiled oil, the oil has a remarkable drying property surpassing that of linseed oil and the dried film is tough, smooth and glossy like tung oil film. Tests have been made for its drying property with different driers and the results are tabulated as follows:

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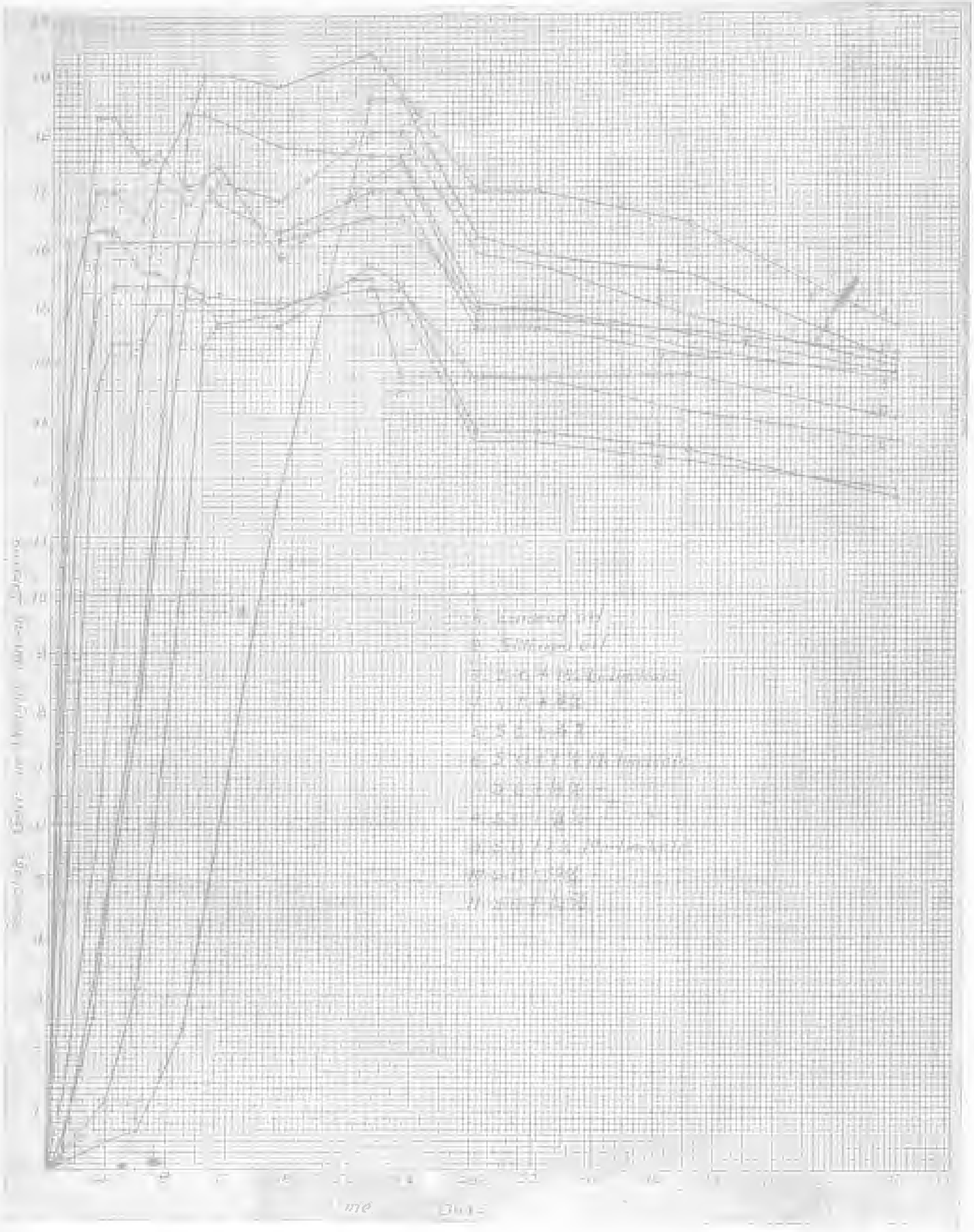
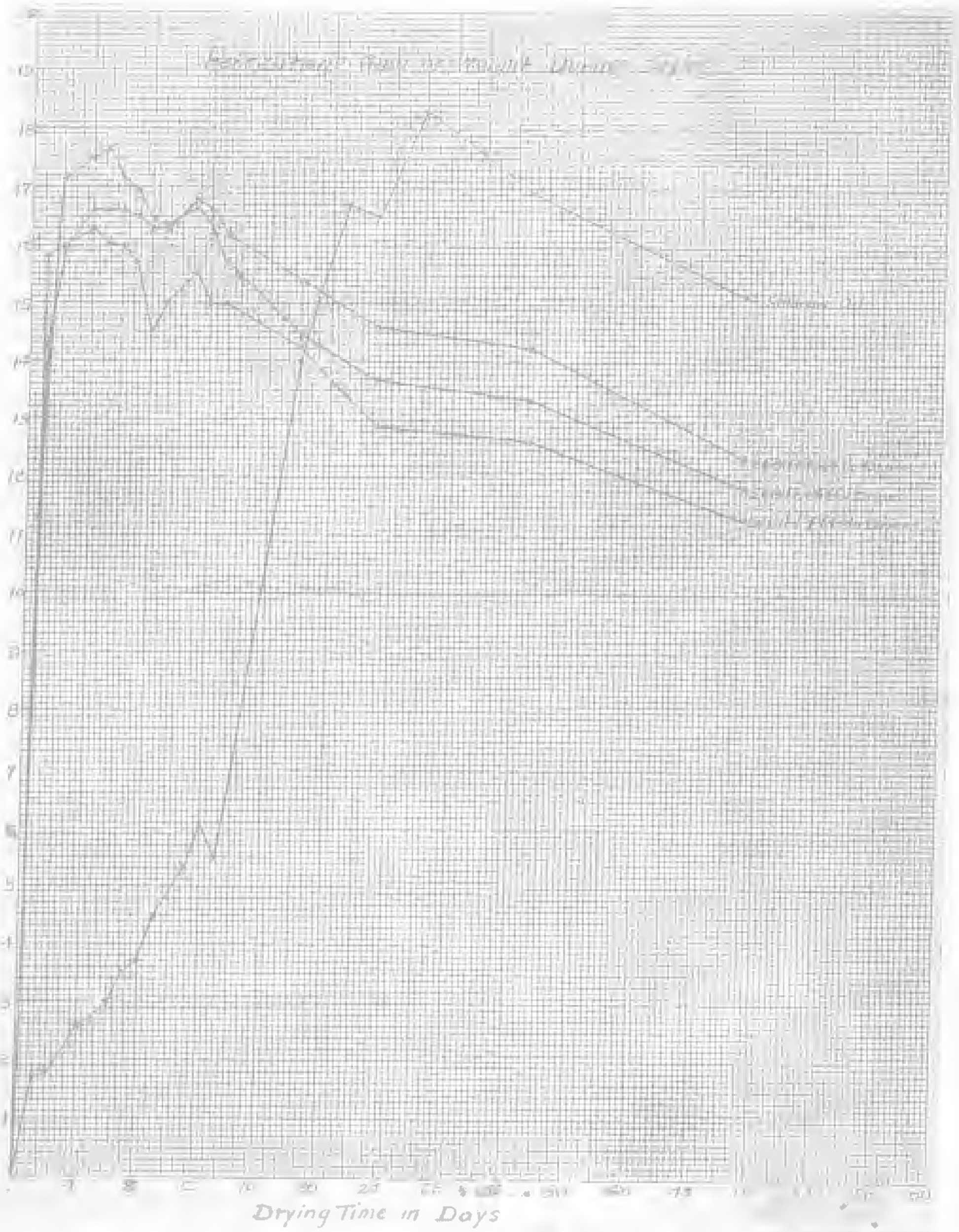
*交通大學研究所油漆報告第二號79頁

Table I. Percentage Gain of Weight During Drying

Time in Days	Linseed Oil	Stillingia Oil (S.O.)	S.O.+Pb-linoleate 1%	S.O.+Pb-linoleate ½%	S.O.+Pb-linoleate ¼%	S.O.+Mn-linoleate 1%	S.O.+Mn-linoleate ½%	S.O.+Mn-linoleate ¼%	S.O.+Co-linolate 1%	S.O.+Co-linolate ½%	S.O.+Co-linolate ¼%
1			1.32	.19	.52	10.74	8.99	4.59	16.11	14.77	12.73
2											
3			5.42	3.13	2.61	15.05	16.11	13.55	16.27	16.96	18.26
4	1.22	.51	8.31	5.16	4.70	15.34	16.11	14.29	16.27	16.96	18.26
6	3.13	.68	14.39	8.65	8.09	15.34	16.11	14.29	15.53	16.46	17.47
7	4.79	.93	17.29	13.08	10.99	15.34	16.11	14.88	15.53	17.16	17.67
9	11.04	2.39	18.31	18.23	15.65	15.34	16.11	14.88	15.11	16.76	17.00
10	14.26	4.00	18.31	18.99	16.70	15.15	16.11	14.88	15.11	17.16	17.17
11	14.61	5.11	18.13	18.99	17.13	15.15	16.11	14.88	14.61	16.76	17.37
15	14.61	11.58	17.75	18.79	16.79	15.05	16.11	14.88	14.78	16.26	15.79
21	15.65	18.57	17.57	19.34	18.00	15.53	16.51	15.45	14.78	16.96	17.17
23	15.30	18.57	17.57	19.34	18.00	15.53	16.51	15.45	14.95	16.96	17.47
28	12.79	16.18	15.04	16.94	15.82	13.71	14.93	13.77	12.62	14.57	14.71
32	12.79	15.84	14.86	16.94	15.65	13.71	14.93	13.77	12.62	14.57	14.71
42	12.52	15.50	14.20	16.39	14.78	13.13	14.46	13.77	12.29	14.07	14.51
56	11.65	13.97	13.64	14.55	13.91	12.65	13.75	12.97	11.79	13.77	14.11
Drying Time in hrs.	96	96	48	48	48	16	22	22	16	16	16


1. Linseed oil
2. Stillingia oil
Time Days


Percentage Gain in Weight During Drying
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
10
20
25
50
75
Drying Time in Days

In view of the above data it is noticed that stillingia oil absorbs more oxygen than linseed oil.

*The function of driers as catalysts varies differently from each other in which manganese and cobalt driers are more active than lead drier. Oils prepared from manganese and cobalt driers oxidize much faster and have better drying property, but after standing and exposing in the air for 3-4 days there is a decrease in weight and after 6-7 days the weights are increased again and then the weights decreased slowly. This is the phenomenon generally occured in the drying curve of oils and some of the noted chemists have already given their explanations as such here and there in articles devoted to drying oils. Gardner has experimented the drying property of linseed oil and his results exactly resemble that of stillingia oil when both are represented on curves. The catalytic power of lead as drier is lower than that of manganese and cobalt. It is so slowly taking up oxygen that it reaches the climax at the end of 8-9 days. Stillingia oil without drier oxidizes very slowly, but the increase in weight is greater than those of oils with driers. In comparison with linseed oil it also gains more weight in same length of time. The amount of drier to be added to stillingia oil depends on the activity of each particular catalyst. For instance same percentage of drier is used, oil with lead linoleate as drier dries very much slower than manganese and cobalt driers. Within the range of 0.1-0.25% of drier added to the oil, the oil oxidizes and dries better with increasing amount of drier, to a certain limit. Above that limit the increase in added drier has no bearing on the drying property. If two or more driers are used in the same oil, the result will be better drying and the amount of drier used can be greatly reduced. Flatt claims that in linseed oil 1.9% lead or 0.1% manganese is used to produce best catalytic effect, but when two are combined and used, only 0.77% lead and 0.002% manganese were necessary to get the same effect. Experiments were made in this connection with stillingia oil.

In the following table it shows that the combined driers have greater effect on the drying of this oil.

Table II. Percentage Gain of Wt. During Drying

Duration in Days	Stillingia Oil	S. Oil+ 1% Pb linoleate+ ½% Mn „	S. Oil+ 1% Pb linoleate+ ¼% Co „	S. Oil+ ½% Mn linoleate+ ¼% Co „
1	1.65	15.85	11.31	14.30
2	1.65	15.99	17.09	16.00
3				
4	2.57	16.28	17.49	16.62

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*Morrell: Chemistry of Drying Oils.

5	2.76	16.06	17.64	16.62
6	2.99	15.99	17.14	16.62
7	2.53	15.69	16.93	16.51
8	3.72	14.52	16.43	16.30
9	4.48	14.99	16.33	16.30
10				
11	5.34	15.55	16.63	16.78
12	6.11	14.99	16.33	16.62
13	5.44	14.99	15.72	16.20
18	14.02	14.23	14.45	15.41
19	15.00			
21	16.69			
23	16.51	12.92	13.69	14.61
26	18.32			
33	16.88	12.63	13.34	14.24
47	15.17	11.31	11.87	12.40

II. HEAT BODYING OF STILLINGIA OIL

Since raw oil is very much too thin to be used in the paints, it requires heat treatment to acquire certain consistency. Experiments were made in this respect to determine the changes of property on heat bodying and to obtain an oil of good working quality. In these experiments stillingia oil was heated rapidly in an oil bath to 250°C. and heat was maintained at that temperature for one hour. Other samples were accordingly made in the same manner except the duration of heating was prolonged to two hours, three hours and four hours.

The physical and chemical properties were studied and the results are as follows:

	Sp. gr.	Acid val.	Sap. Val.	Iod. val.	*Visc@280°	*Color
Untreated	0.9398	1.01	198.4	164.95	A	8
Heating 1 hour	0.9484	1.34	197.9	154.70	H	13
„ 2 hour	0.9563	1.33	198.8	145.25	J	14–
„ 3 hour	0.9628	1.21	199.7	130.00	O	15–
„ 4 hour	0.9733	1.21	203.9	120.10	S	15

It was observed that the viscosity increased very quickly. Though it is not so easily polymerized as China wood oil, it is more easily bodied than linseed oil.

III. USED AS PAINT AND VARNISH VEHICLE

When used in paints, it is found to be a perfect drying oil. Two paints of same pigment composition were prepared by grinding with boiled stillingia oil and boiled linseed oil respectively. They were

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*Gardner's viscometer & color standards.

painted on pine wood panels and all dried in about same time. The panels were then put on roof for exposure test. After a period of one year the panels were examined and found to be in a good condition. They were put back for another four months then checking began to appear on these panels, but still the one with boiled stillingia oil was in a better condition. In the above paints, basic pigments were used and no thickening of the paints was observed. Stillingia oil behaved just like linseed in this case. Varnishes were then prepared from linseed oil and stillingia oil in the same composition and procedure. Varnish made of stillingia oil dried in six hours with glossy hard film, while linseed oil varnish was slow drying and soft. In a series of other experiments in which the stillingia oil substituted for China wood oil in various percentages in the formula, the varnishes gave remarkable properties in every respect. The cooking of varnishes was based on the working procedure in common use. When reduced to laboratory batches, the formulae were as follows:

Formula no.	1	2	3	4	5	6	7	8
Stillingia oil	—	65	65	57.5	57.5	50.0	43	36
Tung oil	65 g.	—	7	7	14.5	14.5	29	29
Linseed oil	7 g.	7	—	7.5	—	7.0	—	7
Lead acetate	0.9 g.	.9	.9	.9	.9	.9	.9	.9
Cobalt acetate	.057g.	.057	.057	.057	.057	.057	.057	.057
Manganese dioxide	.057g.	.057	.057	.057	.057	.057	.057	.057
Beckacite	29.5 g.	29.5	29.5	29.5	29.5	29.5	29.5	29.5
Rosin	5.0 g.	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Turpentine	106.0 cc.	106.0	106.0	106.0	106.0	106.0	106.0	106.0

The oil was heated in a small aluminum kettle to 290°C. in 15 min., then the temperature was maintained for 15 min. for the batch no. 1 until the oil was very heavily polymerized. Driers were then incorporated into the oil. When the foam subsided, resin was dissolved in the oil. On cooling to 180°C thinner was added. For batches no. 2, 3 and 4, 54 minutes' heating at 290°C was required to polymerize the oil to the same consistency as no. 1. For batches no. 5 & 6, 40 minutes' heating was required and for batches no. 7 & 8, 20 minutes' heating only was required. All varnishes dried in 18 hrs. The results of tests are listed below:

Varnishes	(Gardner Holdt) Viscosity	(Gardner Color Standard) Color	Drying Time	(Pfund) Hardness	Gloss	Cold Water test
1	L	12	18 hrs.	.35 mm in 1 min.	98.5%	OK
2	A	15	„	.45	98.2%	„
3	A	15	„	.45	97.4%	„

4	A	16	18 hrs.	.45	97.8%	OK
5	D	14	„	.45	97.8%	„
6	C	14	„	.45	97.8%	„
7	D	13	„	.50	98.2%	„
8	C	13	„	.45	98.5%	„

The viscosity of varnishes was determined by Gardner Holdt Viscometer. Since the time of heating of oils is different in different batches, it is practically impossible to make them all of the same viscosity by using the same amount of thinner. However, the difference of viscosity is not widely apart. In the case of varnish no. 1, it is slightly reduced by adding a little more thinner. Color of varnishes was compared by Gardner's Color Standards. They were nearly all in the same range from light to medium yellow. When spread on glass panels with a thin film they all set dust free in 2 hours and tack free in 18 hours.

The dried films were tested for their hardness by Pfund film hardness tester. Using 50 g weight, varnish no. 1 yielded .35 mm. in 1 min. while others yielded .45 mm and varnish no. 7 yielded .50. Judging from scratches they were equally hard, but the varnishes no. 2-8 were more elastic and flexible.

Ingersoll Glarimeter gave the results of gloss of different varnishes as stated above.

Cold water test had no effect on all varnishes and hot water test had no effect on varnish no. 1 and slightly on others but the whiteness disappeared within two minutes, and as a whole the whiteness on varnish no. 2 seemed to be more persistent.

All varnishes were painted on iron panels with oxide paint as primer coat. They were all thoroughly dried and put in Weatherometer for durability test. Those panels had been exposed for 4 weeks, but no visible effect could be seen on any of them.

By the end of two months all panels showed small blisters appearing on the surface, but no rust could be found anywhere. Gloss was diminished because of the small blisters all over the surface. Judging from the general appearance of these panels number 3 was tha best and number 1 showed most roughened surface.

Summary

1. Stillingia oil absorbs more oxygen than linseed oil.

2. Within the range of 0.1-0.25% of driers added to the oil, the oil oxidizes and dries better with increasing amount of driers to a certain limit.

3. Combined driers have greater effect on the drying of this oil and less driers could be used.

4. Heat bodying of this oil @280°C increases the viscosity immensely. Though it is not so easily polymerized as China wood oil, it is more easily bodied than linseed oil.

5. Paint made from stillingia oil as vehicle is in better condition than linseed oil paint. Oil has no livering action with basic pigment.

6. Varnishes made from stillingia oil are equally good as these made from China wood oil, and in general appearance it is better.

提要

烏桕子油充桐油之代用品

1. 烏桕子油俗稱青油,能吸收氧氣,較胡蔴子油爲多。

2. 青油和以0.1−0.25%之催乾劑,燥性特快;且愈多愈妙。

3. 混合催乾劑效力更大,用量亦少。

4. 在 280°C 所煑之油,時間短而複化易,雖不及桐油之易於複化,但較胡蔴油爲速。

5. 以青油製成之漆,較胡蔴子油製成者爲佳;且與鹽基性粉料,如鋅氧粉等,無變厚作用。

6. 青油製成之假漆與桐油製成者相似。惟二者日久,滿生細泡光澤漸脫,更以後者爲尤。

AN INVESTIGATION ON THE PRACTICAL METHODS OF MANUFACTURING ULTRAMARINE BLUE. I

T. P. JEN (任通寳)

Ultramarine blue has long been used in paint, paper, soap, cotton goods and other industries as a blue pigment. Nothing has ever surpassed it in its quality of resistence to light and alkali. Its brightness of color as well as cheapness of production helps to make it importance to those industries just mentioned. The chief defect of this pigment is probably its sensitivity toward acids.

Prior to the discovery of artificial or French ultramarine in 1828, the only sources of ultramarine blue was the mineral lapis lazuli. To day due to the scientific researches on this subject, the artificial methods of manufacturing have been made possible. On the market there are generally three types of ultramarine blue. These are (1) the Glauber salt or sulphate ultramarine, which has a slight greenish tinge, small covering power, and is easily attacked by alum, (2) the soda ultramarine low in sulphur, which is a pure blue variety, darker than the preceeding, and having more covering power, and (3) the soda ultramarine rich in soda and silica, the darkest variety with a reddish tinge; it has high covering power and is the form most resistant toward alum. At the present time the chief producers of the world are in France, Germany, England and America.

Two systems of manufacturing processes are now in practice. The most up-to-date one is the direct muffle process, in which a mixture of china clay, soda ash, silica, sulphur and resin is charged into a muffle and fired directly to the blue. In direct pot-kiln process, pots are used instead of muffle. The another system is known as the indirect process in which the mixture is first fired with good exclusion of air, and uniform rise of temperature until ultramarine green is obtained. This is subsequently treated with sulphur in a muffle to produce the blue. Products from the kiln are ground and levigated to wash away the soluble salts, meanwhile the blue can be separated into several grades according to their fineness.[1]

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(1) The manufacture of Ultramarine, J. Stewart Remington, Paint manufacture, 3-190 (1933).

A great deal of result of investigation has been published in the past on this subject especially with respect to the general accounts of manufacture and study of the molecular structure of the blue. In recent years, not much advancement has been made on this subject. In spite of many important investigations such as those of Gmelin,[2] Hoffman[3] and Bock,[4] there is still lacking of scientific proof as to the color and constitution of ultramarine blue. As a result of the obscurity of these, the success of manufacture still depends upon technical skill and rule of thumb methods, which rarely appear in the literature. The supreme importance being probably the construction of kiln and control of fire. It is the interest of this laboratory, therefore, to carry out several small scale experiments to make clear the real effects by conditions of burning and composition of raw material upon the qualities of the product, before proceeding the tests in a large kiln.

Raw Materials:—All the following raw materials used in these experiments are of the highest quality obtainable from the local market. They are all fine powders passing through 200 mesh sieve.

1. Kaolin: U.S.P. VIII product of Eimer & Amend, containing 45.9% SiO_2, 37.7% Al_2O_3, and 0.31% moisture.
2. Le Blanc soda: Commercial, dry.
3. Sulphur: Sublimed U.S.P.
4. Silica: Ist. grade silica powder, containing 92.6% SiO_2.
5. Resin: W. W. rosin.

Preparation of Mixture: First method: To assure the thorough mixing and uniform distribution, a thin paste is made by stirring the weighed portions of kaolin and silica into a suitable portion of water, into which the required amount of Le Blanc soda, which has been previously dissolved in water is added. The paste is then evaporated to dryness, and the residue reduced to powder passing through 200 mesh sieve. Sulphur and resin are subsequently added. The mixture receives a final grinding in ball mill for four hours before it is ready for use.

Second method: The various ingredients are thoroughly mixed in a porcelain basin by stirring with a rod for fifteen minutes, then passing through a 100 mesh sieve. This treatment is repeated four times before the mixture is ready for use.

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(2) Schweigg. Fahrb. d. Chem. v. Phys., 1828, 24, 360.

(3) Leibig's Ann., 1878, 194, I.

(4) Zeif, für Angewardte Chemie, No. 6, January 20, 1920.

The mixture used in experiments 1 and 2 is prepared by the first method, while that used in the latter experiments is by the second method.

Method of Calcination: A 4.5 gms. portion of raw mixture is loosely packed in an alundum boat and calcined in an atmosphere of CO_2. The calcination is effected by enclosing the boat in a porcelain tube filled with CO_2, and heated from the outside by means of an electric tube furnace. The porcelain tube is closed by rubber stoppers at both ends. Through one of the stoppers, an inlet for CO_2 and a pyrometer, which directly measures the temperature, are inserted. The stopper at the other end is bored more than half way through, and cut at the side to reach the bore so that the gas within the tube is permitted to force through the incision and not the other way, acting as an one way valve. A sketch of the arrangement is given in Fig. 1. Just before heating, when all parts are in place, a current of CO_2 is passed for three minutes to displace air in the tube, while during the whole period of heating and cooling the CO_2 inlet is well closed.

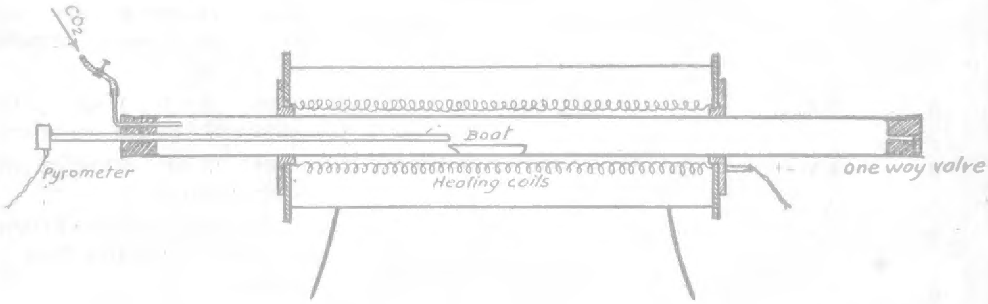

Fig. 1

To facilitate the work on a large number of tests in experiments 3 and 4, the alundum boat has been replaced by several small porcelain boats having one g. capacity. Thus it enables all the mixtures of different composition to be calcined simultaneously in the same porcelain tube.

Experiment 1. Effect of temperature and time of heating upon the color of the product.

A mixture is prepared according to J. S. Remington's formula,[1] which is designed for direct pot-kiln process, and expected to be easily fired resulting in a bright blue. The composition is as follows:

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(1) Paint manufacture, 3-224 (1933).

Kaolin	80 gms.
Sulphur	85 gms.
Le Blanc soda	67 gms.
Silica	12 gms.
Resin	12 gms.

By repeating the calcination with different temperature and time of heating, and noticing the color of the product, a series of data is compiled. They are shown in table 1.

Table 1.

No.	Maximum temp. in deg. C.	Time range in hrs.			Color of product
		Heating from room to max. temp.	Heating at max. temp.	Cooling from max. to room temp.	
1	600	2	½	1½	Dark brown
2	800	2	5	2	Green when fresh from oven, changing into very deep blue upon standing in the air.
3	800	2	8	2	Deep green when fresh, changing into deep blue.
4	800	2	17	2	Light green, changing into deep green.
5	850	2	8½	2	Green when fresh, changing into dark greenish blue.
6	950	3	7	2½	White.

It is noticed from the above table that calcination in CO_2 atmosphere can never produce the blue tinge, but mostly green, which changes gradually into blue of dark shade upon standing in the air at ordinary temperature. The color of the original mixture is yellowish. On heating it changes to brown, then lightens to greenish yellow and finally green when 700-800 deg. C. is reached. Continued heating at 800 deg. C. for 8 hours produces a clear deep green shade. When exposed to air, this changes into a perfect blue although not very bright. Further heating (e.g. for 17 hours) at the same temperature produces the lighter shades, while at 950 deg. C., continuous heating for 7 hours, changes the material into a white powder.

Experiment 2. Effects of air.

In order to investigate the effect of air, the same raw mixture, as used in the preceeding experiment, is calcined in the same apparatus in the presence of a limited amount of air instead of CO_2. The results are summarized in table 2.

Table 2.

No.	Sample calcined	Max. temp. in deg. C.	Total time of heating in hrs.	Remark	Color of product
1	Original mixture.	800	10	Air in the closed porcelein tube is not displaced by CO_2.	Deep green when fresh
2	Green from 1.	650	2	Air in the tube not displaced, a further amount of 50 c.c. forced through the tube at 1 hr. before the end of heating.	Very bright blue; color is permanent.
3	Same green as from 1.	650	4	Same as in No. 2, except the time of introduction of 50 c.c. of air being 2 hrs. before end of heating.	Bright blue, but much deeper than in No. 2; color is permanent.
4	Same green as from 1.	650	6	Same as in No. 2, except the time of introduction of 50 c.c. of air being 3 hrs. before the end of heating.	Light purplish blue; color is permanent.

It becomes clear at this point, that air is strictly necessary in the production of ultramarine blue. By controlling the temperature and time of heating, bright blue of permanent color can be produced from ultramarine green by oxidation with a limited amount of air. But too much oxidation darkens its color or even changes it into a purplish product. (The final product from roasting of ultramarine green with excess of air being a white powder). This is a rather sensitive reaction as compared with the slow process of calcination. In industrial scale of burning, where the kiln is heated to a high temperature of more than 800 deg. C. and is cooled gradually over 10 days, the exclusion of air from the furnace material, especially during cooling, has, therefore, become a very important problem, and in this connection experience and skill are required in such a delicate operation.

Experiment 3. Effect of silica-alumina ratio in the composition of the raw mixture.

To investigate the burning characteristics of high silica and low silica ultramarine, the amount of silica sand added to the mixture is varied, while the amount of kaolin in the mixture is so adjusted as to maintain the weight of silica sand plus kaolin to a constant value. Eight mixtures numbered from G_1 to G_8 have been prepared. They are based upon Remington's formula for 1st. class direct process blue. Table 3 shows their composition in parts by weight.

Table 3.

Sample no.	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8
Silica	0	0.33	0.62	1.15	1.59	1.96	2.30	2.58
Kaolin	6.88	6.56	6.26	5.74	5.30	4.92	4.58	4.30
Le Blanc soda	5.80	5.80	5.80	5.80	5.80	5.80	5.80	5.80
Sulphur	6.40	6.40	6.40	6.40	6.40	6.40	6.40	6.40
Rosin	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84

The results of calcination of these mixtures are summarized in tables 4, 5 and 6.

Table. 4.

(Calcination in CO_2 atmosphere)

Test no.	1	2	3
Maximum temp. in deg. C.	800	800	700
Total time of heating in hrs.	10	16½	17
*Color of product			
G_1	Greenish blue	Dark greenish blue	Dark greenish blue
G_2	Extremely dark blue	Black	Dark blue
G_3	Black	Black	Dark blue
G_4	Black	Black	Extremely dark blue
G_5	Black	Black	Extremely dark blue
G_6	Black	Black	Extremely dark blue
G_7	Partly fused	Partly fused	Greenish dark blue
G_8	Completely fused	Completely fused	Brownish dark blue

*All products are green when freshly taken out from the furnace, those with lower silica content being lighter in shade.

Table 5.

(Calcination with the air in the tube not displaced by CO_2)

Test no.		1	2	3
Maximum temperature in deg. C.		800	650	650
Total time of heating in hrs.		10	20	48
Color of product				
	G_1	Greenish blue	Greenish blue (ashy)	Greenish blue (ashy)
	G_2	Extremely dark blue	Greenish blue (ashy)	Greenish blue (ashy)
	G_3	Black	Deep blue (ashy)	Pale blue (ashy)
	G_4	Black	Deep blue (ashy)	Pale blue (ashy)
	G_5	Black	Dark blue (ashy)	Deep blue (ashy)
	G_6	Black	Dark blue (ashy)	Brownish blue (ashy)
	G_7	Partly fused	Brownish blue (ashy)	Brownish blue (ashy)
	G_8	Completely fused	Brownish blue (ashy)	Brownish blue (ashy)

Table 6.

Test no.		1	2
Max. temp. in deg. C.		800	800
Total time of heating in hrs.		10	13
Remark		Air in tube not displaced, a further amount of 5 cc. introduced 3 hours before the end of heating.	Air in tube not displaced; after 10 hours of heating at 800 deg. C., temp. decreased to 700, and a further amount of 50 cc. of air introduced.
Color of product			
	G_1	Pale blue	Deep green
	G_2	Bright greenish blue	Deep greenish blue
	G_3	Bright greenish blue	Deep greenish blue
	G_4	Deep greenish blue	Dark blue
	G_5	Very deep greenish blue	Dark blue
	G_6	Bluish black	Dark blue
	G_7	Partly fused	Partly fused
	G_8	Completely fused	Completely fused

In the above results of various calcinations a fact common to all of them appears at the first glance: High silica contents causes lowering of fusion point and deepening of color in so far as the products brought about for comparison are calcined under exactly similar conditions. Samples G_7 (Silica/alumina=2.34) and G_8 (Silica/alumina

=2.55), being the highest silica containing mixtures so far tested, have fusion points between 700—800 deg. C. Composition G_1 (Silica/alumina=1.22), in which the silica is solely supplied by kaolin, can still be burned into a pale blue at 800 deg. C.

Experiment 4. Effect of soda content.

By varying the soda contents, four different mixtures are prepared. The compositions are shown in table 7.

Table 7.

(Composition in parts by weight.)

Sample no.	H_1	H_2	H_3	H_4
China clay	5.8	5.8	5.8	5.8
Silica	1.08	1.08	1.08	1.08
Soda	5.0	5.4	5.8	6.2
Sulphur	6.4	6.4	6.4	6.4
Resin	0.84	0.84	0.84	0.84

Table 8 shows their calcination results.

Table 8.

Part 1. Maximum temperature=800 deg. C.
Total time of heating=10 hours.
Remark: Air in the tube not displaced.
Result: All samples have same green color.

Part 2. Greens from part 1 are individually recalcined.
Maximum temperature=600 deg. C.
Total time of heating=2 hours.
Remark: Air in the tube not displaced. This process is repeated until each one has developed their full blue color.

Results:

H_1—Pale blue, H_2—Medium blue,
H_3—Deep blue, H_4—Deep blue,
all colors being very bright.

From the above results, it will be noted that alkali content directly effects the color of ultramarine blue. Deep color corresponds to high content of alkali. According to the original Remington's formula,[1] appropriate amount of soda should be 29%. This corresponds to the composition of sample H_3. Increasing the soda percentage to 31 (sam-

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(1) Paint manufacture, 3-224 (1933), formula No. 4.

ple H_4), the color has no distinct change, while decreasing the percentage to 27 (sample H_2) and 25 (sample H_1), the color lightens a great deal.

Experiment 5. Effect of sulphur.

Some products from the previous experiments are finely ground and washed with water. After drying, they are mixed with approximately their own weights of sulphur powder and recalcined in CO_2 atmosphere. The products are much brighter than before.

Conclusions: The color of ultramarine blue is directly controlled by the following factors:

1. Degree of oxidation during calcination. This is the most important factor and deserves the greatest attention. Yellow or green shade corresponds to insufficient oxidation while charred, purplish, pinkish and white shades are the results of over oxidation.

2. Temperature and time of calcination. Calcination at 800 deg. C. for 8 hours is generally suitable for low silica ultramarines. For high silica ultramarines lower temperature calcination should be employed.

3. Silica and soda contents. The blue shade will be deepened by the increase of either or both of them.

4. Sulphur content. Recalcination with sulphur mostly gives brighter shade.

提　　要

羣青之試製

羣青製造首重色澤,據試驗結果能直接影響成品之色澤者有下列數端

(1)　成品之氧化程度。此點在煆燒時最須注意,若成品呈黃色或綠色必因空氣太少,氧化不足;若已焦黑或呈紫色,淡紅色及白色者則因氧化過度矣。

(2)　煆燒之時間及溫度。製造普通羣青(SiO_2與Al_2O_3之比在2以下者),在800°C煆燒八小時最爲適宜;製高矽羣青則須用較低溫度。

(3)　成品之含鹼及氧化矽量。此二者個別或同時增加均能加深成品之顏色。

(4)　成品之含硫量。淺色羣青經加硫重燒後常呈較佳色彩。

PROPERTY CHANGES OF CASTOR OIL ON BLOWING WITH CO_2 II

T. P. JEN (任通賓)

Continuing the investigation of property changes of castor oil on blowing with CO_2, the writer has performed some distillation experiments with pure ricinolein. Highly viscous but light colored drying oils are obtained. These distillations are carried out under barometric pressure. The object of this investigation is to develope an illustrative laboratory method for the conversion of castor oil into a drying oil through blowing with CO_2. Particular attention has been paid to the simplification and control of the process and color of the product in order to facilitate the work in ultimate analysis which will be done in the next step. The results will be expected to serve as fundamental data for the study of chemical changes occured during the blowing of the oil, and the principle constituent of the oil, which possesses the drying property.

The following experiments may be divided into two parts: The first deals with the ricinolein derived from esterification of pure ricinoleic acid with glycerol, while the second deals with that extracted from the castor oil.

Part 1. To prepare pure ricinoleic acid, 1500 cc. of Chinese castor oil is completely dissolved in 3200 cc. of 97% ethyl alcohol. The solution is cooled in ice bath to below 10 deg. C. for 12 hours. A small amount of white floculent precipitate, being solid glycerides, is removed by filtration in a funnel surrounded by ice water. Majority of the precipitate redissolves during transportation of the mother solution from the flask to the funnel. Therefore, very little is collected on the funnel.

The clear alcoholic solution of castor oil thus obtained is subsequently saponified and precipitated as barium soap. To prepare pure barium ricinoleate, the barium soap is recrystallized from its alcoholic solution four times successively; the final product being a slightly yellowish powder, melts at 104 deg. C. By boiling the purified barium ricinoleate with 4N hydrochloric acid, ricinoleic acid is obtained in the form of a light colored oily liquid. To remove the water emulsified in it, the acid is shaken up with petroleum ether. The acid dissolves. On standing a clear petroleum ether layer separates out. This is filtered and evaporated on water bath in a current of CO_2, until the escaping gas no longer smells of petroleum ether. The acid thus obtained has an acid value of 175.

A portion of 82 gms. of the purified ricinoleic acid is esterified with two third of its equivalent amount (5.6 gms.) of glycerin. The mixture contained in a flask, provided with an air condenser for the distillate, is heated at 230 deg. C. for 5½ hours in a small current of CO_2. Synthesised castor oil is finally obtained, having an acid value of 9.94. It has an orange color.

Another portion of oil is synthesised similarly as above, but this time the distillation is continued with a slow rise of temperature so that the distillate comes out in the rate of one drop per 5 minutes. Above 250 deg. C., the rate of distillation is increased to about one drop per minute, while the temperature rise is kept at a same rate as before. The distillate coming out at first contains mostly water; then it becomes much richer in an oily yellow liquid. White fume comes out in abundance smelling the odor of aldehyde. As the distillation goes on, and when the temperature reaches 295 deg. C., 2 cc. sample of the oil is drawn out for examination. When the temperature reaches 320 deg. C., the oil polymerizes within ½ hour into a brown spongy rubbery like mass. The oil sample taken at 295 deg. C., when spread on a piece of glass, after being mixed with ½ cc. of mineral turpentine and a quarter drop of Pb-tungate in castor oil, dries to touch within 36 hours at 25 deg. C..

Part 2. According to P. Panjutin and M. Rapoport,[1] pure ricinolein may be obtained by extracting raw castor oil three times with petroleum ether containing 10½% aromatic hydrocarbons. One liter of castor oil is extracted six times with its equal volumes of pure petroleum ether. The washed oil is evaporated on steam bath in a current of CO_2 to free from smell of petroleum ether. It is lastly filtered. The oil has a clear straw yellow color and remains clear even after long standing.

The purified ricinolein is distilled in CO_2 current similarly as has been done in *Part 1.* Three distillations have been done, two of them resulting in formation of polymerized mass. The maximum temperature of distillation is 320 deg. C.. Another one has been done with utmost care to chill down the oil just before its polymerization point. The data may be summarized in table I.

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(1) Chem. Umschau Fette, Oele, Wachse Harze, 37, 130-5 (1930); Chemical abstracts, 24, 3665 (1930).

Table I

Purified ricinolein taken=259 gms.
Loss of weight after distillation=63 gms.
=24.3% of the original oil.

Rate of CO_2 current=12 cc./sec.

Time in hrs.	Temp. in deg. C.	Total volume of distillate Water in cc.	Total volume of distillate Oily liquid in cc.	Color of distillate coming out	Remark
0	25	0	0		A white wax like solid deposites at the cold exit of the condenser tube.
1	*200	0	0		
2	217			Brown	
3	229			Brown	
4	244			Brown	
5	240			Brown	
7	275	1½	½	Colorless	
7¾	286			Colorless	Evolution of oily liquid most violent.
8¼	295	2½	19½	Colorless	
10¼	295			Colorless	
10¾	315	3½	69½	Colorless	

The color of the oil becomes gradually bleached on distillation. The final product turns out to be very light colored, but it has a high viscosity. Diluted by twice its volume of mineral turpentine, it has nearly the same consistency as raw linseed oil.

0.2 g. of Pb-Co Soligen drier, dissolved in mineral turpentine, is mixed with 6 gms. of the diluted oil. This, when spread on a glass plate, dries within 31 hours, while raw linseed oil, similarly treated dries within 11 hours. When dried in presence of nitric acid vapor, the former gives a crystallized film just as tung oil will do.

By extracting the polymerized product from the above experiments with ether and alcohol mixture, a viscous oil is obtained. This oil resembles those obtained in part 1 and 2 in all respects.

Conclusions

Part 1. (1) Ricinoleic acid having an acid value of 175 is obtained from castor oil by successive saponification, purification, and acidification.

(2) The acid is heated with two third of its equivalent amount of glycerin at 230 deg. C. for 5½ hours in CO_2 current. Ricinolein thus synthesised has an acid value of 9.94.

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*Oily liquid begins to come out at this temperature.

(3) On distilling under atmospheric pressure in CO_2 current, the synthesised ricinolein is changed into a drying oil when temperature reaches 295 deg. C.. The oil polymerizes at 320 deg. C..

Part 2. (1) Chinese castor oil is purified by washing 6 times with petroleum ether.

(2) On distilling in CO_2 current under barometric pressure, the oil is transformed into a drying oil. The maximum temperature being 315 deg. C.. Further heating will cause polymerization.

(3) This drying oil resembles tung oil in producing crystallized film when dried in presence of nitric acid vapor.

提　　要

煉製蓖蔴子油的性質變化

I (1) 曾用硷化,提煉及酸化等手續自蓖麻子油中提出蓖麻子酸;其酸數為176,

(2) 將此酸與甘油混合（每酸一當量約用甘油2/3當量）在普通氣壓之下加熱至230°C,同時通入炭酸氣,經$5\frac{1}{2}$小時後得合成蓖麻子油精;其酸數為9.94;

(3) 於蓖麻子油精中通入炭酸氣在普通氣壓加熱蒸溜之;當溫度升至295°C後卽變成乾性油,此油在320°C之高溫能起複化作用而結成橡膠狀之固體。

II (1) 國產蓖麻子油用石油醚(Petroleum ether)攪洗至六次後得淨蓖麻子油。

(2) 於淨蓖麻子油中通入炭酸氣在普通氣壓加熱蒸溜之亦變成乾性油其最高熱度祇可升至315°C。若繼續加熱卽起複化作用而結成橡皮狀之固體。

(3) 此法製得之乾性油有一特性頗似桐油卽在乾燥初期中若遇NO_2卽能結成整齊之晶紋漆膜。

A STUDY OF THE PROPERTIES OF ELEOSTEARIC ACID ESTERS FROM POLYHYDRIC ALCOHOLS

T. H. SHEN (沈慈輝) C. F. KUO (郭鍾福)

I. INTRODUCTION

Synthetic oils have been said to be superior to natural oils in uniformity, drying power and other properties. They can be used as substitutes for natural oils in paint and varnish making. All drying oils can be used for this purpose. In the present problem, Tung oil acid is used in the synthesis as it is noted for its superiority in waterproofness and drying.

Tung oil, or China wood oil, consists mainly of the glycerides of eleostearic acid (75%) and oleic acid (25%).[1] The drying property of Tung oil is due to the presence of eleostearic acid.

When eleostearic acid is synthesized with polyhydric alcohols, different types of synthetic oils are obtained. It is in this study, the writer is making investigations into the preparations of these oils and their properties in comparison with natural Tung oil.

II. HISTORICAL

In 1930, a series of synthetic oils had been prepared by Farbenind[2] by heating penta-erythritol, sorbitol, or mannitol, or mixture thereof, along with mono-basic fatty acids of high molecular weight at 150-300°C. The products may be employed as substitutes for linseed oil, as lubricants, etc.

Later, E. I. Du Pont Company[3] had succeeded in the manufacture of synthetic drying oils for paint and enamel use. The resulting oils dry quick, give better gloss, flexibility, hardness and toughness.

In recent years, esters of cellulose, starch, sugars and other carbohydrates with high unsaturated fatty acids had also been prepared by F. Baeyer Co.[4] by treating the carbohydrates with the acid chlorides of the fatty acid.

Last year, L. Y. Sun[9] studied the problem of synthetic oils from Tung oil acid and penta-erythritol and glycerol. According to his results, it is quite promising to synthesize different types of oils from polyhydric alcohols. As his study is only confined to penta-erythritol, the study of other esters will throw more light on the prospects of synthetic oils.

III. EXPERIMENTAL

(1) Preparation of Penta-erythritol

A less laborious and more productive preparation of penta-erythritol as according to Malowan and Corbellini[5] consists of the condensation from acetaldehyde and formaldehyde with lime as condensation agent. According to their idea, penta-erythritol is prepared as follows:

To a mixture of 1 L. H_2O, 560 gm. formalin, and 63 gm. acetaldehyde is added with stirring 47.5 gm. of pure lime freshly hydrated. Steam is passing into the mixture to keep the temperature at 60-65°C. for two hours. It is cooled, and then 170 gm. of cold 50% surfuric acid is added. Precipitated calcium sulfate is filtered, and a saturated aqueous solution of oxalic acid is cautiously added to the hot filtrate, until a filtered sample gives no test for calcium salts. The liquer is decolorized by active carbon, and is concentrated under vacuum to 350-400 cc., crystals are separated on cooling; washed with cold alcohol, and recrystallized from water.

Yield: 90 gm. M.P. 252°C.

(2) Preparation of Eleostearic Acid

Kamataka[8] prepared eleostearic acid by saponification of Japanese wood oil with alcoholic potash and followed by regeneration of this acid with hydrochloric acid. By recrystallization from alcohol, the solid acid was obtained in the form of white, lustrous, laminae. According to his idea, the acid is prepared as follows:

Two hundred gm. of commercial good grade Tung-oil is added to 400 cc. of 95% alcohol and a solution of 42 gm. of KOH in 50 cc. of water is mixed. The mixture is gently refluxed for an hour. The clear solution is then poured into 1500 cc. of 3% aqueous surfuric acid solution. On cooling, α-eleostearic acid will separate out as crystal floating above the aqueous layer which may be drawn off. The acid is washed with about 500 cc. water, filtered and sucked dry. It is then recrystallized from 95% alcohol, saturated at 35-40°C. The pure white rhombic plate crystals are filtered and sucked dry. It is kept in a vacuum dessicator. This is pure α-eleostearic acid free from oleic acid.

Yield: 156 gm. M.P. 44°C.

(3) Preparation of Mannitol

Mannitol is obtained from Haen A. G. Chemisch Fabriken Werk, J. D. Riedal Berlin. The following preparation method is quoted from Isyun Ose[6] & Kenji Mijajis[7] Work:

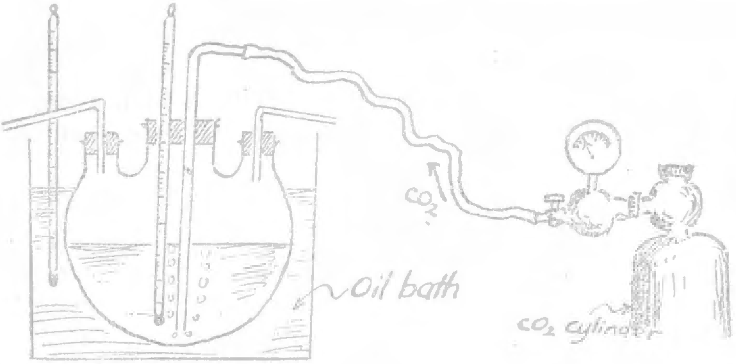
Mannitol fermentation bacteria (Manniticus Sucri) was isolated from acid soil by means of a culture solution containing peptose and fruit juice in agar-agar. Sliced sweet potato is immersed in water, add in KH_2PO_4 to adjust the pH at 5.10-5.15. Let mannitol fermentation occur. Set for 72 hours. Then concentrate the solution by vacuum distillation. The mannitol in residue is extracted out by alcohol. Distil the extraction under vacuum, mannitol is crystallized out.

M. P. 165°C.

(4) Synthesis of Penta-erythritol Eleostearate

Four tenths mol (111 gm.) of fresh α-eleostearic acid and one tenth mol (13.6 gm.) of pure penta-erythritol are mixed in a 250 cc. round bottom, 3 necked flask, 0.05-0.06 gm. of litharge is added as catalyst. One of the mouths is provided with a cork bearing a 300°C. thermometer and a CO_2 inlet glass-tubing, both leading to the bottom; the other two mouths with corks bearing a slit as exit of CO_2 gas. The flask is immersed to the neck in a deep oil bath. The content is heated to 190°C. for 3½ hours and kept stirring constantly by a gentle current of CO_2 gas.

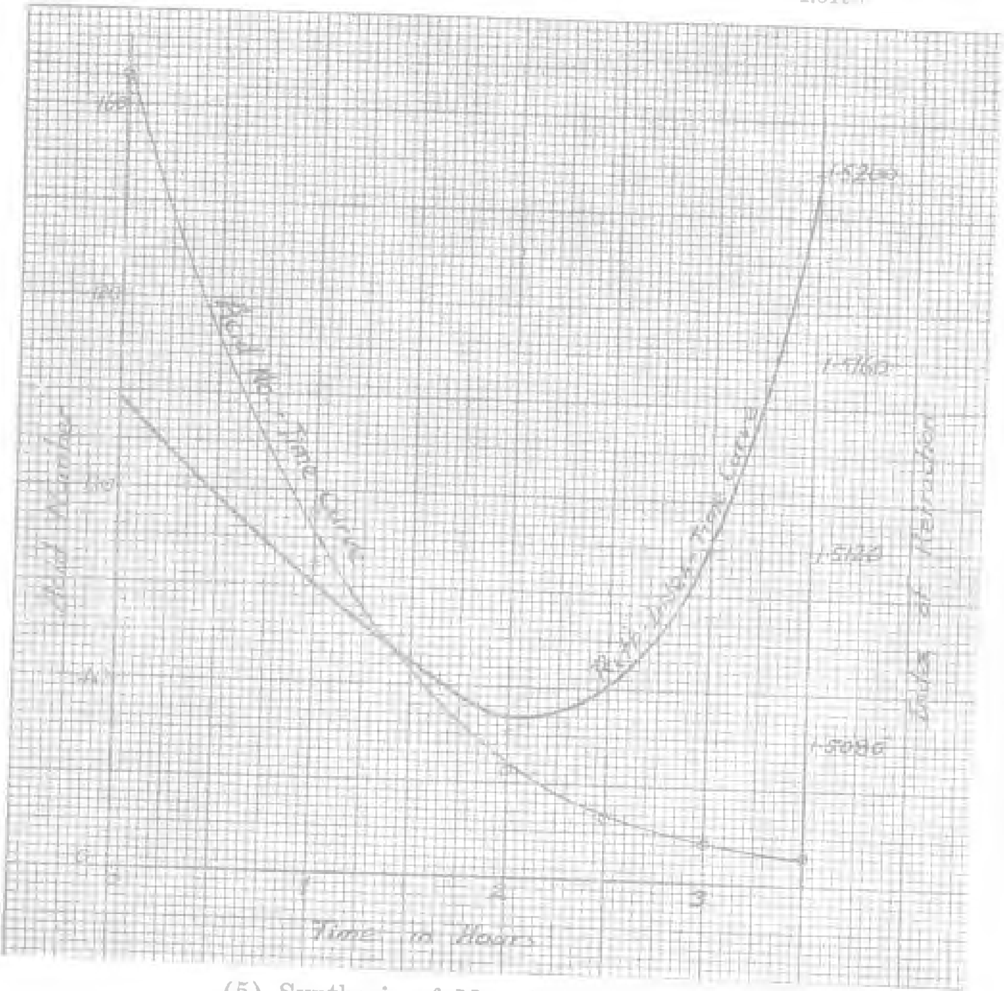
When it is completely esterified, the product is hot filtered.



The degree of completeness in esterification is determined by its acid value and index of refraction. The data is shown as follows:

Time	Acid No.	Index of Refn. (25°C.)
0 hr.	166	1.5146
1.0	75.6	1.5115

2.0	22.1	1 5081
2.5	13.5	—
3.0	8.15	1 5120
3.5	6.05	1.5190



(5) Synthesis of Mannitol Eleostearate

The procedure is same as given in (4), except that it is heated at a lower temperature (180°C.). The amount of materials used is listed below:—

Eleostearic acid	162 gm.
Mannitol	17.5 gm.
Litharge	0.1 gm.

After eight and half hours the viscosity of the fluid increases rapidly, so the heating is stopped in order to avoid polymerization. The acid value during heating is determined at intervals:—

Time in Hrs.	Acid No.
0	168
1	—
2	103
3¼	76.5
4	53.6
5	41.0
6	38.0
6½	31.0
8	21.6
8½	16.0

(6) Preparation of Synthetic Resin

One hundred and twelve grams of Tung-oil (assume 80% glycerol eleostearate) and 18.4 gms of pure glycerol are mixed in a three mouth distilling flask, and 0.5 cc. of sodium alcoholate is added as catalyst. Heat the mixture to 250°C. in an oil bath and pass in carbon dioxide gas. After one and half hours, a homogeneous yellowish fluid is obtained without seeing globules of glycerine suspended in the oil. Then cool down to 150°C. and add in 44.4 gms of phthalic anhydride and reheat the content to 170°C. in carbon dioxide atmosphere until the reaction is complete as indicated by the lowering of acid number.

After three quarters of an hour, the viscosity of the resulting mixture increases rather quickly. When the resin is approaching the point of polymerization, the acid value is still very high. Under such conditions, it is unable to heat the oil any longer in order to complete the reaction without polymerization.

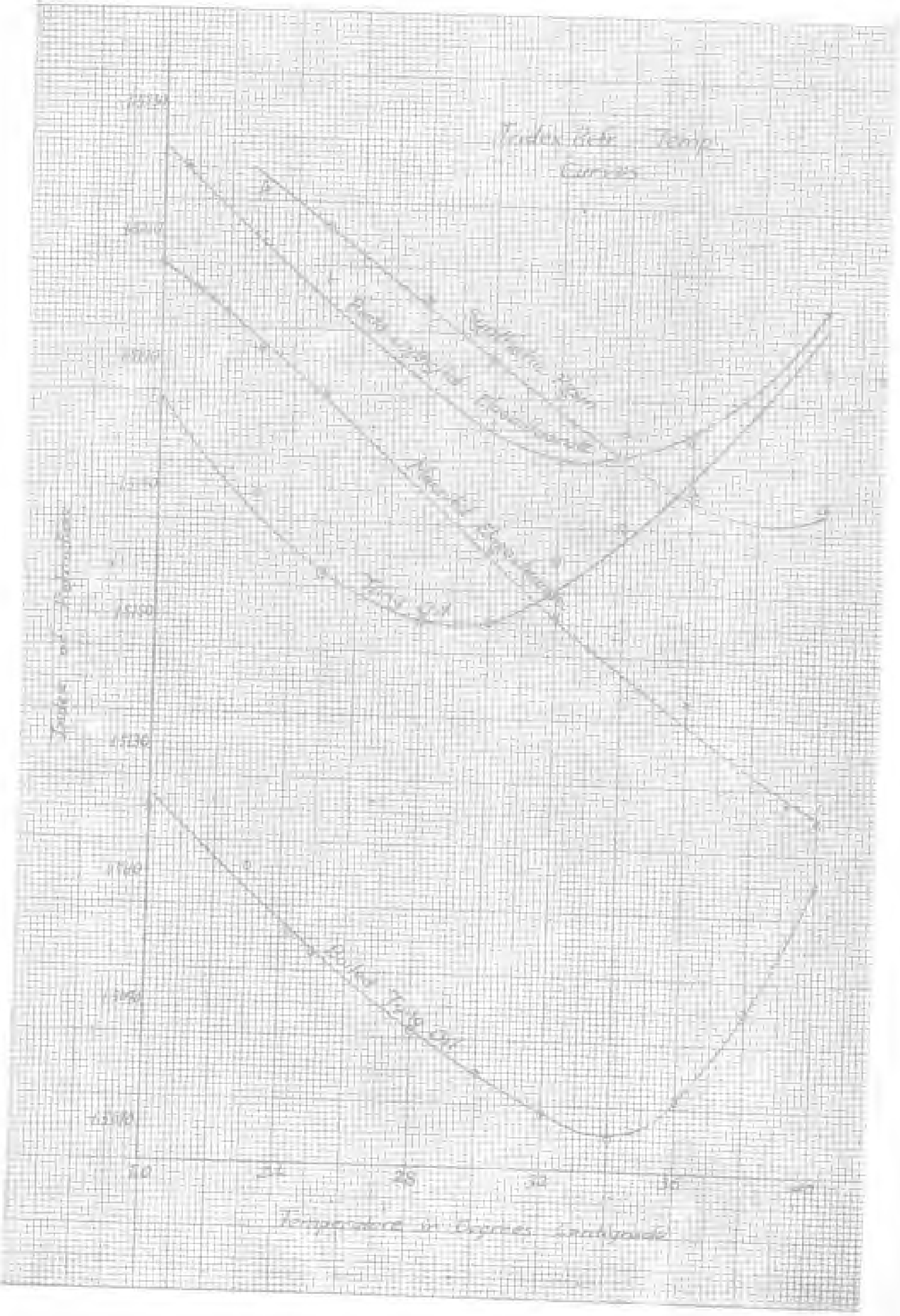
Acid value during heating is shown as follows:—

Time in Hrs.	Acid No.
0	92
0.5	34.8
0.75	28.8

(7) Examination of Products

(*1*) Index of Refraction:

Temp. in °C.	Tung Oil	Boiled Tung Oil	Penta-erythritol Eleo.	Synthetic Resin	Mannitol Eleo.
40	1.5190	1.5110	1.5200	1.5169	1.5120
38	—	1.5090	—	1.5162	—
36	1.5179	1.5076	1.5180	1.5171	1.5138
34	1.5165	1.5070	—	1.5180	—
32	1.5160	1.5074	1.5175	1.5186	1.5151
30	1.5150	1.5080	1.5181	1.5191	1.5161
28	1.5150	1.5086	1.5189	1.5200	—
25	1.5157	1.5098	1.5203	1.5211	1.5185
23	1.5169	1.5111	1.5209	1.5217	1.5192
20	1.5183	1.5120	1.5222	—	1.5205


Index Refr. – Temp. Curves
Synthetic Ester
Recrystallized Eleostearic
Natural Ester
Tung Oil
Boiled Tung Oil
Index of Refraction
20
24
28
32
36
40
Temperature in Degrees Centigrade

(2) Specific Gravity (14°C.):

Tung Oil	0.9418
Boiled Tung Oil	0.9432
Penta-erythritol Eleo.	0.9637
Synthetic Resin	0.9722
Mannitol Eleo.	0.9663

(3) Color (according to Gardner color standard):

Tung Oil	No. 8
Boiled Tung Oil	No. 9
Penta-erythritol Eleo.	No. 11
Synthetic Resin	No. 12
Mannitol Eleo.	No. 11

(4) Acid Value:

Tung Oil	10.8
Boiled Tung Oil	11.3
Penta-erythritol Eleo.	6.05
Synthetic Resin	28.8
Mannitol Eleo.	16.0

(5) Iodine Number (Wijs):

Tung Oil	162
Boiled Tung Oil	151.4
Penta-erythritol Eleo.	146.3
Synthetic Resin	—
Mannitol Eleo.	150.1

(8) Preparation of Varnishes

Varnishes made from prepared oils are cooked according to the following formula:

Beckacite 100	25 parts
Oil	75 ,,
Turpentine	100 ,,
Liquid drier	2 ,,

The Beckacite is heated together with

(1) Tung oil up to 250°C.
(2) Penta-erythritol eleostearate up to 200°C.
(3) Mannitol eleostearate up to 200°C.
(4) Synthetic resin up to 200°C.

Then the batch is cooled down to 180-200°C., and the thinner and driers are added.

The liquid drier used is soligen drier dissolved in turpentine in the ratio 1 to 1, which contains Pb 25%, and Co 2.5%.

(9) Preparation of White Paints

White paints using different oils are prepared:

Lithopone	75	Parts
Oil	25	,,
Turpentine	10–15	,,
Drier	2	,,

Mix the lithopone, liquid drier, with

(*1*) Tung Oil
(*2*) Penta-erythritol eleostearate
(*3*) Mannitol eleostearate

and grind in a roller mill to a fine paste and thin with 10-15 parts of turpentine to a paint consistency.

(10) Comparison of Varnishes and Paints

Using the varnishes and paints prepared, paint over wooden plates, iron plates, galvanised iron plates, and glass plates. The coatings are tested for their drying rate, film hardness (on glass plates), film gloss (on iron plates), elasticity (on galvanized iron plates), cold and hot-water proofness (on iron plates), alkaline proofness (on iron plates), exposure test (on wooden plates, and weathero-meter test (on iron plates).

Film hardness is tested by using Pfund hardness meter. The data obtained are shown by their indentations on loading 150 gms. for one minute. Since the film thickness are different for different varnishes, the results can not be served as a strict comparison of film hardness for different varnishes.

Film gloss is tested by using Ingersoll glarimeter.

The results are as follows:

(*1*) For varnish coating:

	Tung oil	Penta-erythritol Eleo.	Mannitol Eleo.	Synthetic Resin
Drying rate	15 hrs.	8.5 hrs.	4 hrs.	6 hrs.
Film hardness	0.35 mm.	0.48 mm.	0.34 mm.	—
Elasticity	good	good	good	good
Cooled water test	48 hrs. no change	48 hrs. no change	48 hrs. no change	48 hrs. turns white
Boiling water test	15 min. no change	15 min. no change	15 min. no change	15 min. no change
Alkaline test (10% soln.)	5 hrs. attacked	10 hrs. attacked	8 hrs. attacked	5 hrs. attacked
Film gloss	99.0%	97.8%	99.5%	98.7%
Exposure test				
Weatherometer test	3 wks. no defect	3 wks. no defect	3 wks. no defect	—

(*2*) For paint coating:

	Tung oil	Penta-erythritol Eleo.	Mannitol Eleo.	Synthetic Resin
Weatherometer test	2 wks. chalking	2 wks. chalking	2 wks. no defect	—
Exposure test				

IV. DISCUSSION

In the preparation of penta-erythritol, there are some difficulties in recrystallization. In order to hasten the formation of cystals from its concentrated water solution, a plentiful amount of alcohol had been added. Due to much complexity present in the aldehyde condensation, by-product which has low solubility in alcohol is precipitated first, while the principal one had been held up in solution. The by-product has M. P. 98°C. and dehydration takes place above 100°C. forming white crystals which tend to be charred at temperature above 250°C. These facts show that the crystal obtained is not penta-erythritol which should have the M. P. 252°C. However, another crop of penta-erythritol crystals had been found in the mother liquor after several days.

In the synthesis of penta-erythritol eleostearate, the temperature was kept at 190°C. in order to shorten the time of reaction. At this temperature, however, no sublimation of penta-erythritol was observed.

In the synthesis of mannitol eleostearate, the temperature is lowered to 180°C. As mannitol has lower M. P. (160°C.). Thus, during reaction, it is already in the liquid condition, and ensuring good contact with eleostearic acid. Also the color of the product at such lower temperature is lighter. However, in this case, longer time is required to complete the reaction.

In the preparation of synthetic resin from Tung oil, glycerol and phthalic anhydride, the sublimation of the latter one can not be avoided, even when the temperature is lowered below 100°C. Thus the proportion of reactants is difficult to control during the reaction. Moreover, the preheating of wood oil with glycerol during alcoholysis at 250°C. hastens the premature polymerization of the mixture. Due to this difficulty, several trials had been failed. In a latter trial, heating is stopped when the acid value of the resulting mixture reaches 28.8.

It is interesting to calculate the cost of synthetic oils prepared in these ways:

(1) Cost of Penta-erythritol:

formalin	560 gm.	$0.66
acetaldehyde	63 ,,	0.26
lime	48 ,,	0.04
sulfuric acid	85 ,,	0.13
vacuum distillation cost		0.05
	Total	$1.14

Yield: 90 gm.

Cost of penta-erythritol=$1.27/100 gm.

(2) Cost of Eleostearic acid:

Tung Oil	200 gm.	$0.25
Alcohol (95%) (Assume 20% recovered)	320 cc.	0.08
Pot. hydroxide	42 gm.	0.30
Sulfuric acid	45 gm.	0.07
	Total	$0.70

Yield: 156 gm.

Cost of eleostearic acid=$0.45/100 gm.

(3) Cost of Penta-erythritol Eleostearate:

Eleostearic acid	111 gm.	$0.50
Penta-erythritol	13.6 gm.	0.17
Heating cost & CO_2		0.05
	Total	$0.72

Yield: 124.6 gm.

Cost of penta-erythritol eleostearate=$0.57/100 gm.

(4) Cost of Mannitol:

$3.5/100 gm.

(5) Cost of Mannitol Eleostearate:

Eleostearic acid	162 gm.	$0.73
Mannitol	17.5 gm.	0.61
Heating cost & CO_2		0.05
	Total	$1.39

Yield: 179.5 gm.

Cost of mannitol eleostearate=$0.78/100 gm.

Comparison of Cost:

Oil	Tung oil	Penta-eryth. eleo.	Mannitol eleo.
Cost/kg.	$1.25	$5.7	$7.8

Although the cost of synthetic oils are much dearer than that of natural oil, yet they have certain merits over the latter, as in film hardness, drying rate, film gloss and durability, etc.

V. SUMMARY

Workable conditions for synthesizing eleostearic acid and polyhydric alcohols are worked out and ascertained.

The drying rates of synthetic oils are higher than those of the natural Tung oil.

Gloss of varnish films is improved by using mannitol eleostearate.

Synthetic oils are superior to natural oil in alkaline test.

Films of synthetic oils are harder than those of the natural oil.

Under weathero-meter test, varnishes from these oils are all good; while paint with mannitol eleostearate as vehicle is better than that with others.

Cost of synthetic oils is about four or six times as that of the natural oil.

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提要

桐油酸合成油之研究

桐油酸與多元醇,如四元六元醇等,在炭酸氣中加熱至180°C,歷三至八小時之久,可得乾性合成油。其乾燥性,光澤,抗鹼性及韌性均較桐油爲佳,曝露機試驗結果,尤以六元醇爲最佳。惟成本亦昂。

THE PREPARATION OF EMULSION PAINTS FROM SOYABEAN CASEIN

T. H. SHEN (沈慈輝) W. SUN (孫衞)

I. INTRODUCTION

Emulsion paints are emulsions of oil-water type and consist the ingredients, (1) size, (2) oil, (3) emulsifier, (4) pigments and colouring matter, (5) preserving agent and (6) diluent. A stable emulsion is a system containing two immiscible liquids with one of them so intimately and finely dispersed in the other as globules that the proportion of each in any bulk of the mixture is not appreciablly altered by time.

Two pure liquids cannot form a permanent emulsion. An emulsion presupposes the addition of a third substance. The greater colloidal solubility of this substance in either oil or water determines whether the emulsion will be an oil in water or water in oil type. The substance is called emulsifying agent or emulsifier. It is absorbed at the interface of the other two liquids, diminishing the surface tension at the spot, and permitting increased dispersion of one of the liquid in the other.

The common sizes in use are casein, potato, starch and glues or gelatines. Casein gives valuable properties, being non-inflammable and opaque to ultraviolet light, and having good binding properties. It forms insoluble film when formalin is added, and with calcium hydroxide, the casein sol reacts rapidly to form a gel and settles very quickly. Paints prepared from it are washable and will not peel, rub or flake off, and they are water-proof and fire retarding.

The diluent used is usually water and sometimes an emulsified medium without pigment and containing more water. On drying of the paint after being coated on a surface, only water is evaporated off. This saves much cost in using of expensive diluent such as turpentine, white spirit or others in oil paints which is also merely for securing suitable brushing consistency and is lost to the atmosphere afterwards.

The quality of an emulsion paint or oil-bound distemper depends on the materials and recipes and also on the stability, smoothness and fineness of the emulsion. "So far as waterproofness and weathering ability are concerned," as declared by A. A. Jone, "these oil-bound distempers seem to be quite as good as oil paints, and with increasing research on the technical aspects of emulsions, there seems no reason why they cannot be made even better."

Recently, peoples have achieved in extraction of proteins from soyabean cake which Meissel and Böcker refer to as "vegetable casein" and call attention to the points it has in common with animal casein. It must not be unreasonable trying to substitute animal casein with vegetable casein from soyabean in preparation of emulsion paint.

In the present study, it includes:

(1) Extraction of casein from soyabean cake.

(2) Examination of the soyabean casein extracted.

(3) Preparation and comparison of O.W. emulsion from milk and soyabean casein.

(4) Test of emulsion paint prepared from soyabean casein.

II. HISTORICAL

The use of casein in preparing paint in Europe dates back to very early times. M. D. Swartz states that translations from ancient Hebrew texts mention the decorator or painter of the type still existing in a number of European countries, principally in Austria, Hungary, Jagoslavia and the Balkans and Turkey. These texts admonish the housewife to save curd for the autumn visit of the painter. They instruct the husband, the home owner, to go into the hills and bring back the color earths. They admonish the family to have the materials ready to call in the decorator to paint house for the Succoth, which is the ancient Hebrew thanksgiving holiday.

This same system of painting still exists in many villages in the European countries mentioned, and the housewife supplies the curd. In these countries most of the houses are of stone or brick with roofs of thatch slate or tile. The interior walls which are particularly all plastered, receive the painting, while the exterior requires little and no decorating. In the rural towns of Hungary, when painting is necessary, the housewife calls on the painter, makes an appointment for the job, saves enough skimmed milk and prepares sufficient "klabber" or curd for his work. She picks out the colors wanted, which are selected from ochres, umbers, siennas and red oxides. The painter brings the colors and sufficient freshly burned lime, mixes them on the job and goes to work.

The art of using casein in oil paints dates back to the most renowned schools of interior decoration. Milk was permitted to sour and then mixed in the pigments and linseed oil, and used to produce high light effects in portraits in mural decorations. Michael Anglo is said to have used a combination of sour milk, oil and pigment for such a purpose.

In the U. S. the first extensive commercial use of casein in paint dates back to the early part of the nineteenth century, although its use in Germany and England had already been highly developed at a much earlier period. But it is not until this recent years that oil is added to distempers for preparing emulsion paints.

The extraction of proteins from soyabean for the manufacture of soyabean curd (tofu) was started in China in 164 B. C., during the reign of the Emperor Han Wen, by a man named Liu An, the Duke Hwai Nan. Liu An was a great friend of the Buddhist monks, and it seems quite probable that he made this bean curd to provide a change or delicacy to break the monotony of the monastic ration. Soyabean proteins was precipitated from boiled soyabean milk by addition of calcium or magnesium salts.

Extraction of soyabean casein from soyabean cake is a modern industry in Russia.

III. EXPERIMENTAL

1. Extraction of soyabean casein

The method of extraction followed exactly the same procedure worked out by Messrs Yien and Chang.

2. Examination of extracted soyabean casein

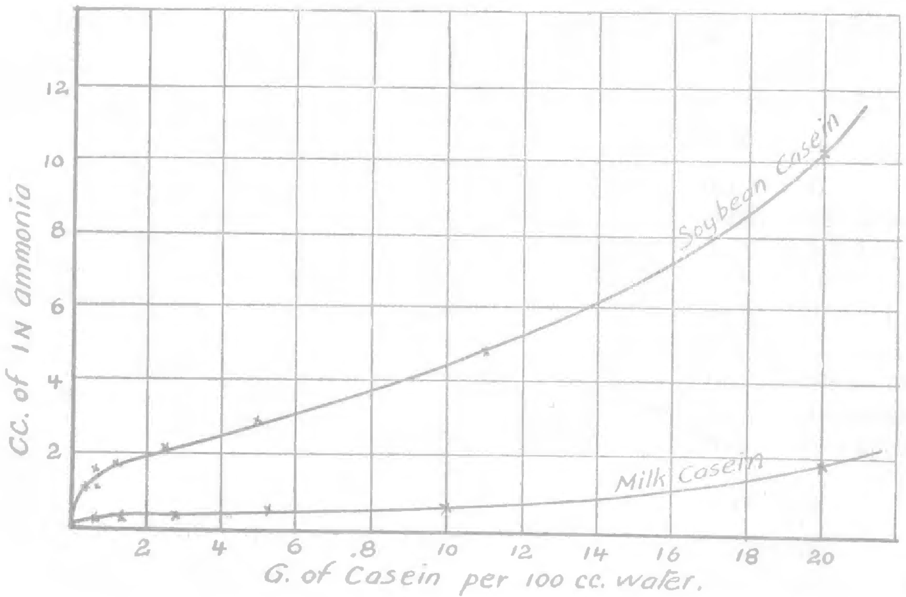
(a) Determination of nitrogen and ash content

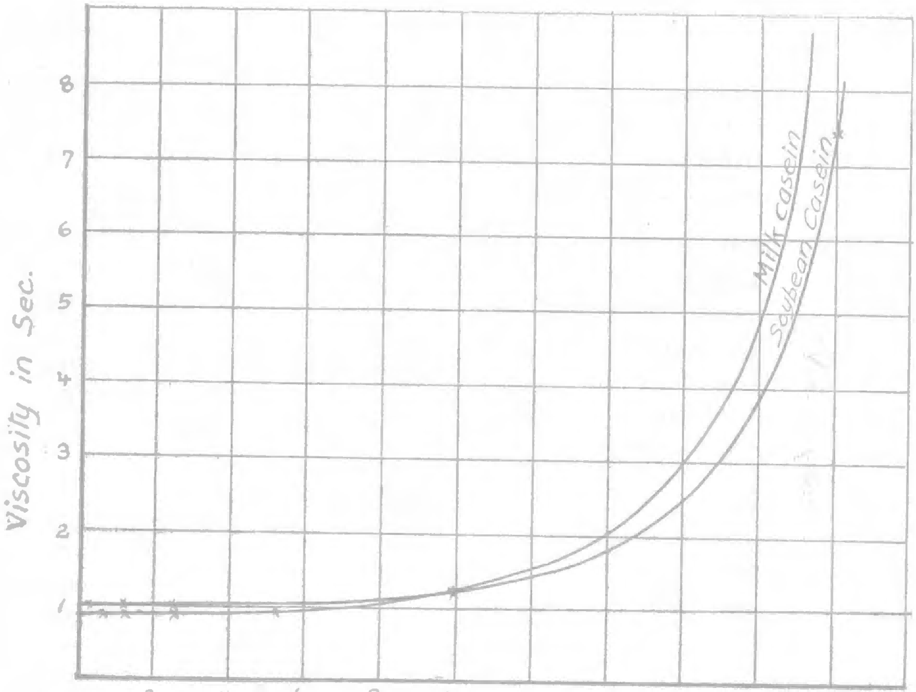
By using Kjeldahl Grenning Method the nitrogen content was found to be 11.9% in the vaccum dried sample and 9.67% in the washed and dried sample.

The ash content was 2.11%.

(b) Physical property of soyabean casein.

The solubility in both cold and hot water was very slight. Mixed with 20% borax, it formed a uniform dark paste. Lime water, Na_2SiO_3, Na_2HPO_4 and Na_3PO_4 were also used but it still failed to dissolve. In ammonical solution it dissolved fairly well. The solubility and viscosity data are represented in the following curves.


12
10
8
6
4
2
cc. of 1 N ammonia
Soybean Casein
Milk Casein
2
4
6
.8
10
12
14
16
18
20
G. of Casein per 100 cc. water.


8
7
6
5
4
3
2
1
Viscosity in Sec.
Milk casein
Soybean Casein
2
4
6
8
10
12
14
16
18
20
G. of Casein per 100 cc. water.

It was yellowish in color, odorless and non-inflammable.

The properly dried casein did not putrify on storing.

3. Preparation of emulsion

In the preparation a proper amount of ammonia sufficient to dissolve completely the soyabean casein was required to give a good emulsion. It showed that 2.5—5 g of soyabean casein dissolved in 100 cc of .0225-.045 f NH_4OH gave good emulsions with 40-60% of linseed oil. Various other experiments were performed by varying the casein content, concentration of ammonia, and linseed oil content, but they all failed to give good results. It was observed also that no emulsifying agent should be added to the solution, because the soyabean casein is a good emulsifying agent besides of its being a binder.

4. Preparation of emulsion paints

Several formulae had been experimented. Emulsion paints of milk casein were also prepared for comparison:

No. 1.

soyabean casein	2.5 gm
water	100 gm.
ammonia	4 cc.
boiled linseed oil	100 gm.
lithopone	160 gm.
oil of merbane	2 cc.

For milk casein,

milk casein	8 gm.
water	100 gm.
ammonia	3 cc.
boiled linseed oil	100 gm.
lithopone	160 gm.
oil of merbane	2 cc.

No. 2.

casein (soyabean)	12 gm.
water	140 gm.
ammonia	3 cc.
lime	15 gm.
tung oil-linseed oil mixture	60 gm.
whiting	75 gm.
clay	20 gm.
ethyl alcohol	40 gm.

ethyl acetate	20 gm.

(This formula fails to give a good paint)

For milk casein,

dextrine	4 gm.
milk casein	24 gm.
lime	30 gm.
trisodium phosphate	2 gm.
tung oil-linseed oil mixture	60 gm.
whiting	110 gm.
clay	30 gm.
ethyl alcohol	120 gm.
ethyl acetate	60 gm.

The tung oil-linseed oil mixture consists of tung oil 10 parts, boiled linseed oil 10 parts, turpentine 12 parts and manila copal 8 parts.

No. 3 A.

casein (soyabean)	12 gm.
ammonia	3 cc.
water	120 gm.
boiled linseed oil	40 gm.
whiting and clay (55:15)	40 gm.

No. 3 B.

casein (soyabean)	12 gm.
ammonia	3 cc.
20% sodium acetate solution	20 cc.
water	120 gm.
boiled linseed oil	40 gm.
whiting and clay	40 gm.
ether	2 cc.

No. 4.

soyabean casein	3 gm.
ammonia (6 N)	2 cc.
borax	3 gm.
water	100 gm.
tung oil-linseed oil mixture	100 gm.
lime	12 gm.
lithopone	85 gm.
clay	23 gm.

The precautions for preparing these paints are as follows:

(1) The oil-water medium should be well prepared. Soyabean casein is first peptized to form a homogenous sol in water and the remaining undissolved residue filtered out. Oil or varnish is then agitated with the sol to form a well dispersed emulsion.

(2) The paint cannot be ground in a flat stone mill or cone mill in which water is pressed out and a sticky, thick paste of oil-pigment mixture is left in the mill. The emulsion is destroyed during grinding.

(3) The pigment should be "pugged" for a long time with the oil-water medium to secure intimate incorporation with the medium and to get a uniform and homogenous paint. Otherwise an uneven mass will be formed which will separate out a small amount of oil on the surface with pigments settling to the bottom.

(4) The pigments should be ground to extreme fineness and dried thoroughly. The purposes of grinding and drying are exactly same as prolonged pugging.

(5) It is proper to grind the emulsion paint in a ball mill for some time, but I have not tried.

(6) On dilution of the paint with water, thorough stirring is also necessary. Water or oil-water medium rich in water is added slowly and the whole thing stirred violently and continue the stirring after finishing the addition for a long time to secure uniformity and homogeneity. Otherwise an uneven coating on the surface to be painted will be formed.

(7) The diluted paint gives still better results when stand for one or two days before applications.

Effects of different constituents in the emulsion paints:—

a. Medium or vehicle

(1) Ammonia. Soyabean casein is peptized to form a uniform sol by soaking with hot water at 70°C and ammonia for half an hour. The last trace of residue which remains undissolved is filtered out through glass wool. Oil is then added.

It is better to use a mixture of ammonia and other alkali salts such as borax, sodium phosphate or sodium acetate so that the latter serves also as a buffer salt and the *p*H value of the solution will not be too high. For an emulsion paint with an oil-water medium of *p*H value more than 8 separation into two layers may take place.

Another method of adjusting *p*H value is by neutralizing the sol with boric acid.

(2) Lime. Lime is to give a body to the paint. It converts the casein sol into a jelley, and makes the oil-water medium very plastic and

thick. The plasticity and thickness depends upon the concentration of casein and amount of lime used. It is better to add lime to the paint vehicle at same time with pigments. Grind and mix thoroughly the lime with mixed pigments. Add the mixture to the medium while stirring and continue the stirring for one quarter to half an hour till the mixture grows thicker and thicker and whole thing forms a uniform paste. Lime when added preceeding the addition of pigments will make the vehicle very plastic with which the intimate incorporation of pigments becomes very difficult.

b. Pigments

The pigments say lithopone and clay or whiting and clay are mixed and ground at first. The pigments are then dried before added to the vehicle. The process of drying has same function as prolonged stirring during addition of pigment to the oil-water medium as to prevent formation of clots. Lithopone has adventage over whiting of having good tinting power and covering power. Clay is to help the suspension of pigments in medium.

c. Preserving agent

Without preserving agent, the paint is easily coated with dark green mold on the surface when put in a dark and damp place for one week or more days. Trace of formaldehyde, oil of merbane or carboric acid prevents this growth of mold.

d. Other substances

Ether—generally a little froth is always present on the surface of casein solution which cause pin holing of the paint films made from it. A trace of ether added to the paint serves to remove froth and make the painting very smooth.

Alcohol and ethyl acetate—according to formula No. 2, alcohol and ethyl acetate are used. But this does not give any good result. Though the milk casein paint with formula No. 2 can be worked smoothly under flat stone mill, it dues to form a coating which possesses no adhesive power on surface applied, being easily scrubbed off by hand and washed away by water. Furthermore, it destroys the water oil soyabean casein emulsion.

5. Examination of paints

The paints according to different formulas are painted on iron plates, wood, and cement surfaces, and examined.

On iron plates, red spots of iron rust show on the surface after one day and peel off all the paint after four days.

On cement, the paints dries more quickly but give a less adhesive coating and can be scrubbed off easily.

On wood surface, it gives a firm, smooth coating.

On brick, the property is intermediate between that on wood and on cement.

Generally two coats are required to give a perfect surface, a primary and a secondary coatings.

(1) Color and appearance

Paint No. 1	slightly yellowish
Paint No. 3A	pale white
Paint No. 4	with a little greenish shade.

Paints of milk casein are comparatively whiter.

The paints are velvety in appearance and give no gloss. The variation of oil water ratio does no effect.

(2) Covering power

Covering power of paint No. 2 on wood is 158 square feet per pound of paint. That of milk casein is 173 square feet.

(3) Drying property

The paints dry to form a soft film after one day and dries completely after one week.

(4) Washing property

Both milk casein and soyabean casein paints with formulas 1, 3A, 4 are water-proof. When immersed in water for one week no change takes place on the surfaces. And the coatings cannot be scrubbed down when rubbed by cotton waste with water.

(5) Inflammability

When burned with a flame the paints become charred but are not inflammable.

(6) Heat resistance

Heated to 90°C in an oven the paints turn slightly to brownish color after one hour. After 4 days milk casein paints peel off but the soyabean casein paints still give no change. The soyabean casein paints remain as perfect coats after a week.

(7) Roof test

After three weeks' exposure paint No. 3 of soyabean casein cracks while others remain no change after 6 weeks from April 24th to June 8th.

IV. Summary

1. Soyabean casein can be used as a substitute for milk casein in the manufacturing of emulsion paint.

2. Optimum conditions for making emulsion: using 2.5 to 5 gm. of soyabean casein per 100 cc. water with 2.25 to 2.9 cc. of 1 N ammonia, soaking at 70-90°C till a good colloidal solution is formed, filtering out any residue remaining undissolved through glass wool, adding not more than 2.5 cc. of 1 N boric acid to every 100 cc. of the solution to adjust the *p*H value, then running in slowly equal volume of oil or diluted varnish (with turpentine) while stirring and shaking the oil-water mixture intermittently for 1½ hours.

3. Optimum conditions for making emulsion paints: grinding the pigments, e.g., lithopone, clay and calcium hydroxide to very fine, mixing them thoroughly, drying, and then adding them slowly to the vehicle with rapid stirring and pugging the whole thing for ½ to one hour.

4. Superiority or inferiority to milk casein emulsions and paints: soyabean casein forms emulsions very easily without using additional emulsifying agent; the paint prepared from it is more resistant to heat than that from milk casein and just same as that from milk casein is water proof and non-inflammable. But the paint from soyabean casein is not as white as and less adhesive than that from milk casein. The vehicle is more alkali in property than that from milk casein due to need of larger amount of ammonia to dissolve the soyabean casein than milk casein.

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提　　要

豆酪素製水粉漆之試驗

豆酪之性質與牛乳酪相似,所以可供製造水粉漆之用。按試驗所得耐熱與耐水性俱佳,惟色較黃。配製之法:以豆酪二・五至五公分溶於水一百公分;另加二・五至二・九公分之IN阿姆尼水,並加硼酸使氫離子指數之價在八之下,然後將等量之胡麻油漸漸搗入,成乳狀液體。製漆時應用粉料,須求乾而細,則易於磨成乳化水粉漆。

A SUMMARY OF THE STUDIES ON SOYABEAN CASEIN

H. Hsieh (謝惠) T. P. Jen (任通寶) P. K. Chang (張丙官)

Many years ago Meissl and Bocker have referred the glycinin as "vegetable casein", and called attention to the points that it has in common with animal casein. Only recently interests have been arisen among the industrial circle to recover this protein from soyabean cakes, in which its content is more than 30%. Several patents can be found in the literature, differing from each other especially in the choice of extraction medium. Water, saline solution, ammonium hydroxide, and 0.5-1.5% potassium hydroxide have all been used. Among these, the first two have been abandoned due to their low efficiency. Potassium hydroxide is considered the most common, while ammonium hydroxide has been claimed uneconomical because of the difficulty and expense of ammonia recovery. The use of potassium hydroxide has the danger of resulting in degradation of the proteins due to its comparatively high alkalinity.

Two other substances, which have not been considered and yet seem suitable for the same purpose, are sodium carbonate and sodium bicarbonate. The present paper is to study the possibility of substituting these two substances as media and their efficiencies as compared with that of potassium hydroxide. The isoelectric point and industrial applications of the vegetable casein are also ascertained. A knowledge of the former is especially important when complete coagulation of the protein from its solution becomes necessary.

I. RAW MATERIAL

The raw material used in these experiments is soyabean cake obtained from the local market. Several analyses of the cake give the following average composition:

Moisture	8.73 %
Ash	5.32 %
Oil	6.89 %
Protein	45.30 %.

II. APPROXIMATE DETERMINATION OF THE ISOELECTRIC POINT OF SOYABEAN CASEIN

A water extract of the soyabean cake was prepared by grinding and digesting the powdered cake with fresh water. The residue was separated out by filtering through a cotton bag. The filtrate, being a milky liquid, was finally centrifuged to remove the last trace of suspended impurities.

Equal portions of the water extract were acidified with varying amounts of acetic acid to cause different degrees of coagulation of the protein in the extract. This was done in a set of Nessler's tubes so that amounts of protein separated out can be directly compared by measuring the depth of protein precipitate accumulated upon the bottom of the tubes after complete settling. At the same time the *p*H value of the liquid in each tube was measured by means of a potentiometer. It was found that the approximate isoelectric point of vegetable casein or rather the optimum acidity of the water extract of the cake for the coagulation of vegetable casein in it was 4.6 in *p*H value, as it can be seen from the results tabulated in table I, that the coagulation of protein at that acidity is most complete.

Table 1

Tube no.	1	2	3	4	5	6	7	8	9	10	11	12
Mg. Eq. of HAc present	0	0.353	0.544	0.907	0.968	1.089	1.210	1.814	2.42	4.24	7.86	12.10
*p*H value of liquid	7.34	5.58	5,04	4.59	4.50	4.43	4.34	4.14	3.99	3.78	3.54	3.34
Depth of precipitate in cm.	0.1	0.1	2	2.2	2	1.9	1.9	2	2	1.9	1.9	1.9
Turbidity of supernatent liquid.	m	d.m.	t	c	s.t.	s.t.	s.t.	s.t.	t	t	t	t

Notes: Total volume of liquid in each tube is about 70cc.
Abbreviations employed have the following significance, m, milky; d.m., dense milky; t, turbid; c, almost clear; s.t., slightly turbid.

III. KOH, Na_2CO_3, AND $NaHCO_3$ AS SOLVENTS FOR VEGETABLE CASEIN

(1) KOH as solvent.

In order to avoid the loss of KOH due to saponification of oil, the oil contained in a portion of finely powered beancake was removed by extraction with CCl_4. The oil-free powder thus obtained was divided into ten parts and digested separately with KOH solution of varying strength. To determine the extent of dissolution of protein in each case, equal portions of clear liquid were taken out from every mixture, acidified with acetic acid and followed by addition of saturated solution of barium chloride to coagulate the protein completely. The coagulated protein was then filtered, washed with alcohol and finally dried and weighed. Table 2 shows a comparison of the results.

Table 2

Sample no.	1	2	3	4	5	6	7	8	9
Oil-free cake powder in gms.	7	7	7	7	7	7	10	10	10
Strength of potash sol'n. in % KOH	0	0.05	0.10	0.15	0.30	0.50	0.80	1.00	1.70
Mg. eq. of KOH present	0	2.68	5.35	8.02	16.06	26.8	42.8	53.5	90.9
*p*H value of sol'n.	6.14	8.81	10.33	11.06	11.91	12.29	12.54	?	12.85
Grams of casein obtained from 50 cc. of the extract.	0.111	0.186	0.325	0.402	0.487	0.440	0.636	0.600	0.691

(2) Na_2CO_3 and $NaHCO_3$ as solvents.

The procedure, used to test the relative degrees of dissolution of vegetable casein in these two solvents, was the same as stated in the preceeding paragraph. The results are shown in tables 3 and 4.

Table 3

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Strength of alkaline water in % Na_2CO_3	0.20	0.60	0.79	0.99	1.47	1.96	2.92	3.85	4.76	5.66	7.41	13.8	16.7
G. of casein obtained from 10 cc. extract	0.073	0.137	0.199	0.267	0.325	0.350	0.355	0.375	0.394	0.341	0.348	0.276	0.269
*p*H value of solution	7.03	8.63	9.04	9.33	9.61	9.77	10.00	10.00	10.06	10.11	10.14	10.28	10.21

Table 4

Sample no.	0	1	2
Strength of alkaline water in % $NaHCO_3$	0	1.96	3.85
Grams of casein obtained from 10 cc. extract	0.021	0.097	0.109
*p*H value of solution	5.21	8.17	8.69

Notes: (1) In all cases, powdered cake used=10g.
alkaline water added=100cc.

(2) Due to saturation, concentration of $NaHCO_3$ solution beyond 5.6 is impossible.

The relative efficiencies of KOH, Na_2CO_3, and $NaHCO_3$ as solvents for the vegetable casein, according to the results so far obtained, are best shown by the curves in Figures 1, 2, and 3.

From these curves the following conclusion may be drawn:

(a) The optimum concentration is 1.5% for Na_2CO_3, 0.15% for KOH and 2.0% for $NaHCO_3$.

Fig. 1

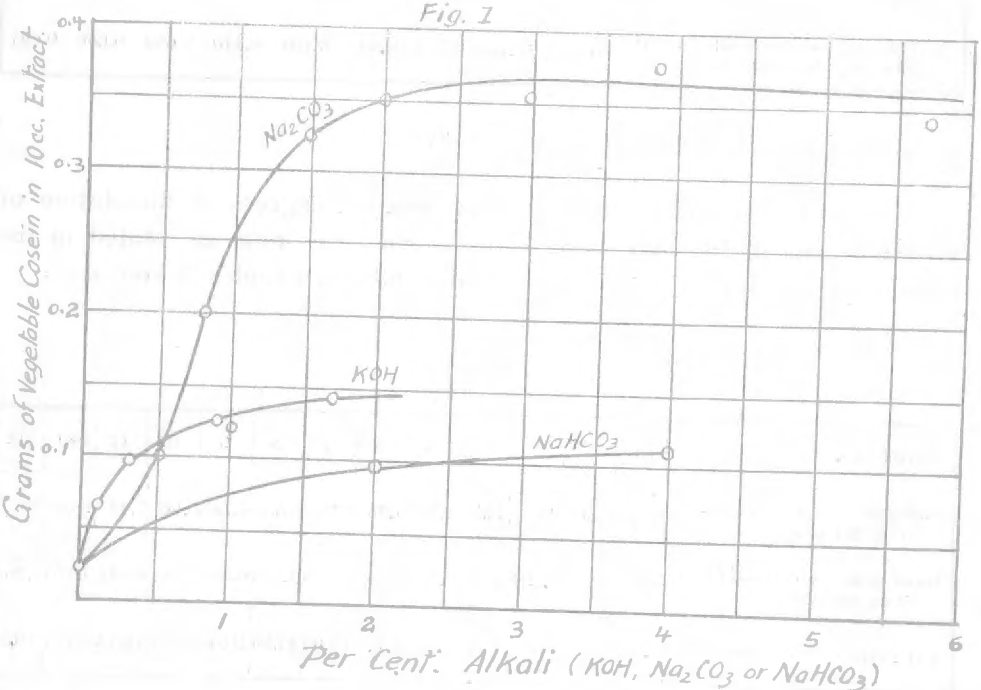


Fig. 2

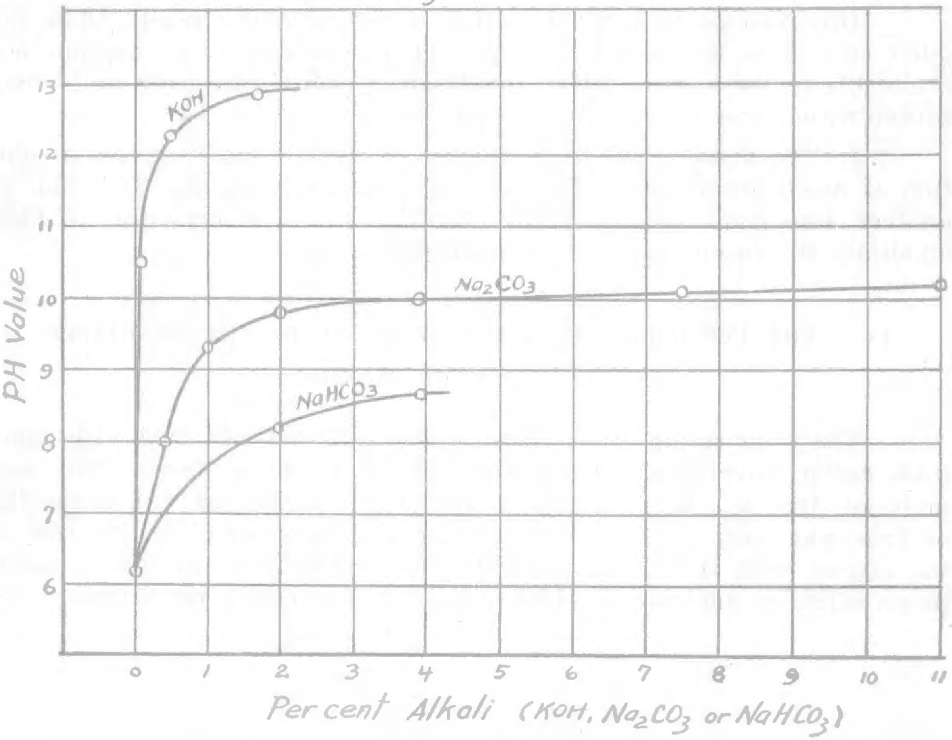
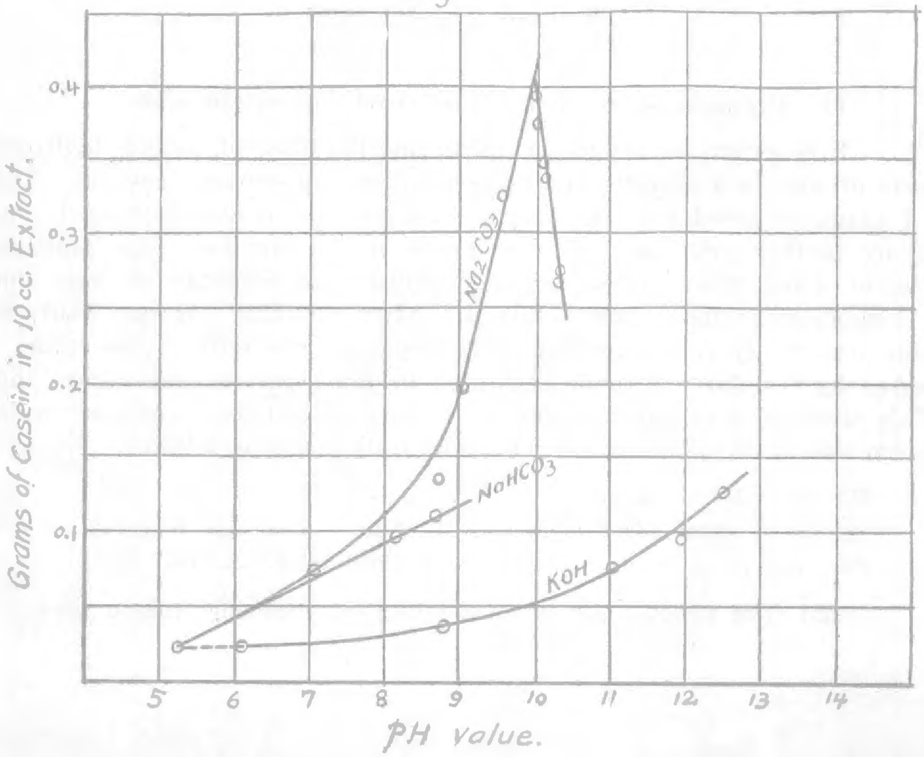

13
12
11
10
9
8
7
6
PH Value
KOH
Na_2CO_3
$NaHCO_3$
0
1
2
3
4
5
6
7
8
9
10
11
Per cent Alkali (KOH, Na_2CO_3 or $NaHCO_3$)

Fig. 3


0.4
0.3
0.2
0.1
Grams of Casein in 10cc. Extract.
Na_2CO_3
$NaHCO_3$
KOH
5
6
7
8
9
10
11
12
13
14
PH value.

(b) Na_2CO_3 is a much better solvent for the casein than the other two, since it dissolves a larger amount of casein; an amount not attainable in the case of KOH and $NaHCO_3$, no matter how high their concentration way be raised. (see fig. 1)

(c) To dissolve the same amount of casein, Na_2CO_3 gives a solution of much lower alkalinity than the other two (see fig. 3). This is another important advantage of Na_2CO_3, since in presence of high alkalinity the casein is apt to be degraded.

IV. THE POSSIBILITY OF THE UTILIZATION OF THE VEGETABLE CASEIN IN GLUE MAKING

The preparation of magnesium glue and wet-mix glue with vegetable casein have been investigated and the products tested. The raw material, that is, the vegetable casein, was obtained by extracting the oil-free cake with 1.5% Na_2CO_3 solution and subsequent acidification of the extract with HCl. The product, when dried, is a pale yellow amorphous solid, an analysis of which gives the following composition.

Moisture	3.44 %
Ash	7.35 %
Protein	76.94 %
Oil	0.63 %
Phosphorus	0.54 %
Sugar	1.54 %

(1) Preparation of magnesium-vegetable casein glue.

Five grams of vegetable casein and 0.6 gms. of sodium hydroxide were ground in a porcelein mortar to a fine homogeneous powder. Then 0.7 grams of powdered magnesium oxide was added and thoroughly mixed by further grinding. To one gram of the mixture, thus prepared, 3cc. of warm water was gradually added with constant stirring until a homogeneous mass was obtained. After standing for one hour, the glue was ready to be applied. The shearing strength of this glue, as tested by standard method, amounted to 178.5 pounds per square inch. This strength was found to decrease enormously when a greater or less water was used. The actual results of testing are as follows:

Mixture taken in gms.	1	1	1	1	1	1
Volume of water added in cc.	2	3	4	5	6	7
Shearing force in lbs./sq. in.	82.7	178.5	168.0	122.5	66.7	77.4

(2) The preparation of wet-mix lime-vegetable casein glue.

A mixture of the following composition was prepared by mixing thoroughly the various ingredients all in powdered form.

Casein	5	gms.
NaOH	0.3	„
CaO	0.98	„
Borax	0.3	„
Water glass	1.5	„
Phenol	0.1	„

To prepare the glue a portion of the mixture was stirred into a suitable amount of warm water. Glue containing 2.8 cc. of water per gram of the original mixture was found to possess highest shearing strength. It amounted to 445 pounds per sq. in. had the pressure on the test block during drying of the glue been above 4 lbs. per sq. in.. Similarly as before, the shearing strength decreased enormously when more or less water was used. The complete results are as follows:

Mixture taken in gms	1	1	1	1	1	1	1	1
Volume of water added in cc.	1	2	2.8	3	4	5	7	8
Shearing strength in lbs./sq.in.	0	80	445	283	201	144	88.5	19.2

V. SUMMARY

(1) The soyabean cake, obtained from the local market, has been analysed and is found to have a protein content of 45.30%.

(2) Isoelectric point of the soyabean casein is found to be around *p*H 4.6.

(3) KOH, Na_2CO_3, and $NaHCO_3$ are compared for their efficiency as solvents for the soyabean casein. Na_2CO_3 is found to be the best. 3% of this salt in water solution will dissolve the maximum amount of the protein, but 1.5% is sufficient for the practical purposes.

(4) Magnesium-vegetable casein glue and wet-mix lime-vegetable casein glue have been prepared. When proper amounts of water are used during preparation, the former gives a shearing strength of 178.5 lbs. per sq. in., and the latter 445 lbs. per sq. in..

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提要

從豆餅中提取豆酪及其應用之研究

從豆餅中提取豆酪,已有多種成法;其最大不同處,爲豆酪溶劑之選擇。苛性鉀,用者最多,惟因其礆性强,故製出豆酪,皆略有變性。炭酸鈉與炭酸氫鈉,礆性較弱,似甚合宜;惟此法尙未經採用。本篇特就此二者,與苛性鉀,作一比較試驗,以定其優劣。並附帶檢定,豆酪之同電點及豆酪應用於製膠之可能性。所得結果如下:

(1)本市所售豆餅,據化驗結果,約合45 30%之蛋白質。

(2)豆酪之同電點,約爲4.6。

(3 豆酪之溶劑,以炭酸鈉之溶液爲最佳;尤以濃度在1.5−2.0%者,爲最適宜。

(4)含鎂之豆酪膠,與含鈣之豆酪膠,均經配製。如加適當之水配用,前者可得每方寸178.5磅,後者可得每方寸445磅之抗切强度。

PREPARATION OF LOW VISCOSITY NITRO-CELLULOSE

K. T. Lin (林厥達)

The reduction of viscosity is worked along three lines:

(A) Before nitration
(B) During nitration
(C) After nitration

(A) Treatment Before Nitration

Conditions Reagents	Conc.	Temp.	Time	Vol. of soln. Wt. of cotton
$NaOH + KMnO_4$	$NaOH = 0.2\%$ $KMnO_4 = 0.4\%$	room temp.	until no $KMnO_4$ color	soln. = 200 cc. cotton = 4 gms.
Dil. NaOH	1%	100°C	0.75 hr.	„
Dil. H_2SO_4	1%	100°C	2.00 hrs.	„
$Fe(NO_3)_3$	5%	90°C	3.00 „	„
Autoclave	pure water	180°C	3.00 „	„

Results Reagents	Viscosity of cellulose	% of reduction for cellulose	Viscosity of nitro-cel.	% of reduction for nitro-cel.	Result
$NaOH + KMnO_4$	18 sec.	79.3%	105 sec.	0	B.N. + A.N. −
Dil. NaOH	24 „	70.6%	„	0	B.N. + A.N. −
Dil. H_2SO_4	10 „	88.5%	„	0	B.N. + A.N. −
$Fe(NO_3)_3$	11 „	87.4%	„	0	B.N. + A.N. −
Autoclave	9 „	89.7%	„	0	B.N. + A.N. −
Non-treated cellulose	87 „		„		

Note: B.N. = before nitration; A.N. = after nitration.

The viscosity of cellulose is measured by burette; while the viscosity of nitro-cellulose is measured by the falling ball method.

Conclusions

(a) The viscosity of cellulose can be reduced greatly.

(b) The viscosity of nitro-cellulose is independent of the viscosity of cellulose.

(B) DURING NITRATION

The acid mixture used consists of:

HNO_3	(sp. gr. 1.36)	100 parts
HNO_3	(sp. gr. 1.47)	50 „
H_2SO_4	(sp. gr. 1.84)	100 „

Twenty to thirty parts of the acid mixture to one part of cotton is used. The temperature is kept at 55°C. for three quarters of an hour. The viscosity of the resulting nitro-cellulose is 105 seconds measured by the falling ball method. However, the temperature is the first importance; the higher the temperature (up to 55°C.), the lower is the viscosity of the product.

(C) TREATMENT AFTER NITRATION

The nitro-cellulose is refluxed in alcohol and alkaline solutions at the temperature of 80°C. for fourteen hours. The resulting nitro-cellulose has the viscosity of 10.5 seconds, with reduction for 90% to the untreated nitro-cellulose.

Conclusions

The longer the time of reflux, the greater is the degree of reduction of the viscosity.

There are two important points needed to be improved:

(a) The solubility of the treated nitro-cellulose in solvent mixture seems to be decreased a little bit.

(b) A part of nitro-cellulose is lost in reflux.

提要

低粘度硝棉之試製

試驗方法,以各種藥品將棉絨泡煑,結果粘度自八十七秒減至九秒,若以混合酸在55°C.時煑之,所得硝棉之粘度爲一百〇五秒。倘用鹼液及酒精,在80°C蒸溜之,得十·五秒之硝棉。如延長蒸餾時間,則粘度尚可減低,惟一部之硝綿亦必因而消失。

LACQUER SOLVENTS FROM FUSEL OIL

H. W. TING (丁憲祜)

Fusel oil consists of the high boiling alcohols—propyl, butyl and amyl alcohols. They are used in the lacquer formulae to smoothen the film and to prevent blushing. They are used as diluents but not solvents. The solvents most generally used are butyl acetate and amyl acetate. In fusel oil, we extract amyl alcohol, and then it is esterified to amyl acetate. A rough method esterifies the fusel oil directly. The mixture of esters are then usable as lacquer solvent. It can be purified by fractionation also.

Procedures

(1) Test of raw material—fusel oil. Determine specific gravity, boiling range, spirit content etc.

(2) Fractionation of fusel oil—different alcohols are obtained.

(3) Esterification of the product from (2)—desired solvents are obtained. They are rather pure esters.

(4) Esterification of fusel oil—Direct process.

(5) Fractionation of the product from (4)—mixture of esters separated and purified.

(6) Tests of intermediate and final products—specific gravity, solution power of nitrocotton etc.

Every procedure is repeated for the two given samples—one from 美龍 and one from 中國

提　　要

從什醇油中提煉硝棉漆溶劑之研究

曾將我國酒精廠之殘液,分溜得醇類數種,經酯化而得各種純酯。另以什醇油直接酯化,亦得什酯;再經分溜,仍得如前之各種純酯。由是加以檢定,並研究其對於硝漆之溶解性。本題所用原料係美龍與中國二廠出品。

THE STUDY OF CHINESE LACQUER

N. A. CHOW (周怒安)

1. Analysis of raw lacquer has been done.

   The results are as follows:

	Szechuen	Yunan	Kweichow
Urushiol %	71.27	56.80	55.60
Gum arabic %	8.63	13.95	11.92
Moisture %	20.10	29.25	32.48
Specific gravity	1.028	1.089	1.121

2. General study of its physical and chemical properties and the reaction with different reagents were made.
3. Influence of increasing temperature to the rate of drying was studied and with the increase of temperature up to 80°C., the rate of drying was hastened.
4. Influence of solvents was studied and benzene gave the better film in appearance than other solvents.
5. An optimum conc. of driers had been sought and 0.2% Mn was the best.
6. The loss of wt. of lacquer was studied.
7. Formaldehyde condensation product obtained.
8. Vulcanizer product formed and the relation between the temperature and the length of time required to obtain the product also studied.

提　　要

生漆之研究

本試驗曾取生漆分析,並檢定其特性。其乾燥速度,與氣候溫度有關。若酌加催乾劑,則乾性尤快。其他工作如和硫乳化,發酵褪色等,亦經作初步試驗。

MISCIBILITY OF TREATED CASTOR OIL WITH MINERAL OILS

Y. KWEI (桂雍)

Owing to the high viscosity and its slight changes with temperature, Castor oil is valuable as lubricating agent. It has long been used in railways and shops, and is still considered indispensable for certain types of aeroplane motors. There are available on the market several brands of lubricants consisting of a mixture of Castor oil and mineral oil; of these the best known is "Castrol". Since Castor oil is ordinarily not miscible with mineral oil, special treatment is necessary to prepare such a product. A method of long standing consists in heating the Castor oil at 300°C for 1 or 2 hrs. to secure a decomposition of 10-20%. The process has been modified in various ways by many patentees. The object of this work is to ascertain the optimum condition for such a treatment with the use of a dehydrating catalyst.

Experimental

The raw oil was purified by first heating to 50°C and then treating the filtered oil at 50-60°C for 2 hours with 5-10% NaOH solution. After settling and washing, the oil was decolorized twice with 1% Norite A at 110°C. The purified oil was clear and brownish yellow in color.

The catalyst used was anhydrous aluminum oxide (Al_2O_3). The oil, either raw or purified, was heated to various temperature with or without stirring. The volatile decomposition product was removed by blowing in a current of CO_2. Samples were taken for examination at various intervals or at the end of the experiment.

After standing the treated oil for several days, the supernatent layer was freed from suspended matter by filtration after the addition of an equal amount of petroleum ether to reduce its viscosity. The clear oil obtained after distilling off petroleum ether was then tested for miscibility with equal volume of spindle oil.

The results from the various runs may be tabulated as follows:—

Table I.—Time of heating variable; with CO_2 and without stirring.

Serial No.	Conditions of Heating			Characteristics of Products	
	Amt. catalyst	Temp. °C	Oil	Final	Intermediate
1	¼%	250°, and raised to 260° after 4 hrs.	refined	Sample at end of 5 hrs., brownish color. Slight odor. Perfectly miscible.	Sample at end of 1, 2, 3, 4 hrs. not entirely miscible but miscibility increasing with time of heating.
2	½%	250°, and raised to 260° after 4½ hrs.	raw	Sample at end of 6 hrs. similar to No. 1.	Samples at end of 1½ & 3 hrs. are not entirely miscible. Sample at end of 4½ hrs. miscible.

Table II.—Time of heating variable; with CO_2 and with mechanical stirring.

Serial No.	Conditions of Heating			Characteristics of Products	
	Amt. catalyst	Temp. °C	Oil	Final	Intermediate
3	½%	250°C	refined	Sample at the end of 7½ hrs. heating brownish, with slight odor and little change in viscosity. Completely miscible.	Samples at the end of 1½, 3, 4½, hrs. not entirely miscible. Sample at end of 6 hrs. miscible.
4	¼%	260°	do.	Sample at end of 7½ hrs. same as No. 3.	Samples at end of 3 hrs. miscible.
5	$\frac{1}{10}$%	250°	do.	Sample at end of 7½ hrs. same as No. 3.	Sample at end of 6 hrs. miscible.

Table III.—For comparing the difference between highly refined oil and raw oil. Time of heating variable; with CO_2 and with mechanical stirring.

Serial No.	Conditions of Heating			Characteristics of Products
	Amt. of catalyst	Temp. °C	Oil	
6	½%	260°C	highly refined	Oil after 7 hrs. very slight odor and color; not entirely miscible.
7	¼%	260°	raw (acidity 18.6%)	Oil at end of 3½ hrs. brownish color and slight odor. Miscible.

In the experiments without stirring, uniform mixing of oil and catalyst may not be secured because of the tendency of Al_2O_3 to settle down to the bottom of heating vessel. So the results in Tables I are not so reliable as those in Tables II and III.

From the data given above, the following conclusions may be drawn:—

(1) The amount of catalyst has little effect on the rate of reaction as can be seen from No. 3 and No. 5.

(2) The rate of change at 260°C is very much higher than that at 250°C.

(3) Raw oil seems to change faster than the refined oil for reasons not definitely known at the present time.

This work is being continued and further data will be given in the subsequent reports.

提 要

蓖蔴油製潤滑油之研究

蓖麻油可供潤滑劑之用,飛機馬達應用尤廣,市上兼有礦物油攙和品出售。但平常蓖麻油與礦物油不相混合,須採特殊製煉方法方有效。本題目的在以氧化鋁爲去水接觸劑,檢定最適宜製煉手續。經初步試驗結果,得探知下列三點:

(1)接觸劑多少與蓖麻油在礦物油中可溶性之增加無大關係。

(2)分解速度在攝氏260度較在250度增加甚多。

(3)未精煉之油分解較速,理由未明。

解除染織廠應用井水之硬度方法

丁嗣賢

按紡織印染工廠所用之水,最忌含有過量硬度;尤忌含有鐵質。蓋硬度及鐵質,均易使出品有「走色」,「發黃」,「發暗」,及「顏色不勻」之弊。此種工廠用水,所含鐵質,爲量須極少,方能適用;水含鐵質達一千萬分之二(0.2 P.P.M.或$\frac{2}{10,000,000}$),已嫌不佳,若達一百萬分之二(2 P.P.M.或$\frac{2}{1,000,000}$),則非經提淨手續,不能應用。

現據送來新老二井水化驗單各一紙,新井水每一百萬分水中含有定質總數444·00,不定硬度362.85,總鐵質2.00,中等分量滓渣;硬度固高,而鐵質尤嫌過量,核其品質,應列「劣等」。老井水每一百萬分水中含有定質總數424.00,不定硬度335.50,鐵質0.34,微量滓渣;硬度較新井水略低,鐵質則低減尤多,約爲新井水六分之一,品質實較新井水爲優,然仍應核居「硬水」之列。

解除方法　據上化驗推論,欲使該水適合該廠之用,匪特應除去該二水之硬度,尤應除去其鐵質,（老井水鐵質較少,或可不除,勉强應用,然究不如除去爲妙。）其法爲

（一）用「幫浦」,（卽抽水機）增加水之壓力,將水打入蓮蓬頭式（略如雨浴所用,惟孔須特小。）噴水器或噴霧器（可用普通夏日噴洒草地之噴霧器,較噴水器爲佳。）,由噴霧器直向上噴入空中,水卽自然吸收空氣而落下,噴

霧器下設一淺水池以承之（池係水泥做）,復由此池流入較深之解硬池,經過相當時間,鐵質自然沉澱,變爲黃褐色物質。

（二）水流至解硬池後,俟其將滿,將水道關閉,停止水流,加入適當分量之石灰乳〔石灰乳製法,取上等生石灰（塊灰）一份,置於適當器皿之中,如鐵桶,水缸,磚池,洋灰池等,加水三分（卽一斤石灰加水三斤）,俟石灰化碎,再加水和成稀漿,卽成。但須隨製隨用,並須用上等塊灰,否則解硬力損失。〕,充分攪拌廿分鐘或半點鐘,不定硬度自然分解,然後停止攪拌,聽其澄清沉澱,澄清之水,鐵質及硬度已除,卽可隨時由放水管取用矣。若再使之經過沙濾池,則水可更清,但非絕對必要。

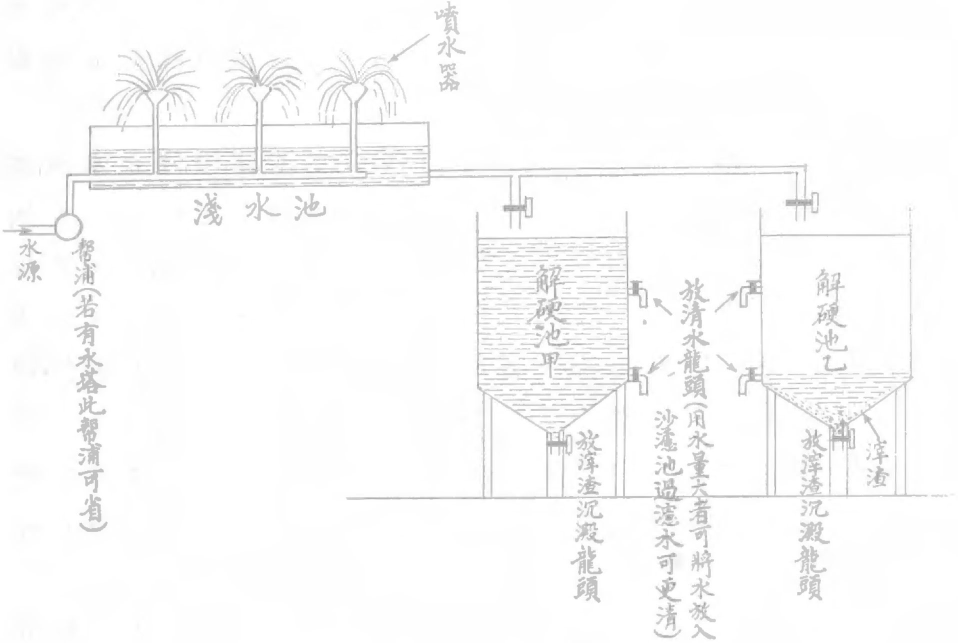
（三）所加石灰乳,約合每一百担新井水（一萬市斤或五千公升）用上等乾塊石灰二斤六兩餘（2.39市斤,卽市斤2斤6兩餘）,每一百担老井水用上等乾塊石灰二斤三兩餘（2.21市斤,卽市斤2斤3兩餘）。

（四）所用石灰應含氧化鈣百分之八十五;若含氧化鈣較高（質地較好）,則應照比例核減;若含氧化鈣較低（質地較劣）,則應照比例增加。若上海五洲固本皂廠所用之石灰,其成分約爲氧化鈣百分之八十五。

（五）解硬池中積聚沉澱,因含有鐵質,故呈黃色。清水用盡,可隨時由池底放出,棄去。

（六）解硬池大小隨意,應視用水量而定。但應有二個,以便輪流使用,甲池加石灰乳解硬時,乙池供給清水;乙池加石灰乳解硬時,甲池供給清水;如此輪流使用,巡迴不息。若有必要,亦可多設數個。

（七）各種設備附略圖於下:



解除硬度及鐵質設備圖

（八）水由淺水池流入解硬池後,不加石乳灰,用水汀將水煑沸約一小時,亦可將硬度除去,但不及用石灰解除之充分,且熱力消耗,其代價較用石灰爲昂,故若無餘剩價廉之水汀,仍以用石灰乳爲宜。

油漆常識

油漆與傳熱之關係

沈慈輝

現代建築,需用油漆甚繁,而對於取色與傳熱之問題,則少研究,取用時隨心所欲,漫無標準,例如建築物之內外墻壁,熱水汀,油池等,應用油漆,皆與人生之舒適,燃料之經濟與儲油之損失等,關係至大此乃應有之常識,故特擇要述之。

傳熱之方法,計分三種,卽對流法(Convection),傳導法(Conduction)及直射法(Radiation),若熱氣從物質之熱處傳至冷處者,稱爲傳導,隨氣體或液體之流動而傳熱者,稱爲對流,由以脫之波浪鼓動而傳遞者,稱爲直射,直射法祇有被射擊之物體受其熱,而太空則不受其熱,對流與傳導之傳熱方法,俱藉物質而傳達,所以大致相同,能合稱爲一,簡而言之,傳熱方法祇有傳導與直射二種,而傳導法又爲傳熱之主要者。

水汀　無論應用何種傳熱器,由傳導而生之熱,約占百分之八十,由直射而生之熱,約居百分之二十,然而如在熱水汀上,髹以油漆一塗,間或幾塗,其塗數雖增加,但由傳導所生之熱則相等,愛倫氏曾在熱水汀上,髹漆一塗至十四塗,而其傳導所生之熱則相同,所以傳熱時,由傳導所生之熱,俱無關係,所差者亦惟此百分之二十之熱,由直射而生者耳,普通裝置水汀,往往髹以金銀色之磁漆,豈知藉此漆直射所生之熱,不如白色遠甚,據試驗報告,由直射所生之熱之最强者爲白色,最弱者爲黑色,奶色紅色綠色黃色銀色及棕色,則居其間,五節之水汀,髹白漆者,其由直射所生之熱,與六節水汀髹銀色漆者相等,換言之,銀色水汀有少供給約 1/10 之

熱量,亦即多費1/10之金錢也,玆將司登賽爾氏(Stansel)以各漆試驗結果列下,以資參考。

油漆種類	反射力(生鐵=1.0)	油漆種類	反射力
奶黃磁漆	1.03	白油漆	.98
白磁漆	1.01	黃磁漆	.97
生鐵	1.00	平光綠漆	.96
奶黃油漆	1.00	灰磁漆	.96
綠磁漆	.99	金色磁漆	.76
淺綠油漆	.99	銀色磁漆	.72

房屋　應用油漆,亦以白色爲佳,因其在夏日之下,不易受熱故也,太陽光線,經以脫而直射於房屋之墻面,假使牆爲白色,或淺淡之色,則大部熱光爲所反射,屋內溫度較低,自覺涼爽,至於冬季,則墻面宜易黑色或深色,如人之衣服然,但房屋之時時易色,殊非經濟而簡易,所以日常所見者,非白即紅,皆宜於夏季而不適於冬季,求其理,蓋因夏日之熱不易避,而冬季屋內之溫度,則易於控制也,然而油漆之顏色,既宜於夏,則不宜於冬,若屋內溫度較低,仍須多用燃料以取暖,此亦不可不計及也,油漆與建築材料溫度之關係,列表於後:——

建築物內之空氣溫度(室外溫度爲82°F)

漆色	鐵箱內之空氣溫度	木	鐵	水泥	水泥漆	紅磚	紅磚漆
無漆	102°F	114°F	126°F	108°F		114°F	
白漆	102	104	106		102°F		96°F
奶色漆	103	110	110				
銀色漆	104	114	114				
橘黃漆	107	118	118				
紅漆	108	126	122				
灰漆	110	122	120				

藍漆	108	120	122
綠漆	109	124	126

房屋之外墻,塗漆之後,非特可以減低溫度,抑且能避潮濕,例如未漆之墻,在暴雨之後,吸水約千分之一百十五,而已漆之墻,祗吸千分之五,相差甚鉅,所以現代建築,都採用水門汀漆,以避潮濕。

屋內之光綫,與墻壁之顏色,亦頗有關係,强別爾氏曾以各種顏色,作比較試驗,在一室之中,塗以一色之漆,懸燈於頂,燈下置一桌,塗以氧化鎂,然後以測光器量其光綫,如是者白色,粉紅,黃,綠灰等各色,均經試驗,玆將各漆之反光性列表如下:

漆名	反光比數
銀鏡	.89
白漆	.88
淺綠漆	.69
淺黃漆	.74
灰漆	.68
金銀色磁漆(1)	.68
金銀色磁漆(2)	.42

從上表觀之,可知白色或淺色之漆,可供給較爲充足之光綫,金或銀色之漆,皆不適用也,室內髹塗油漆,除增加美觀清潔,充足光綫之外,又有阻止空氣吹入墻壁之功用,例如胡蔴子油二塗,可阻百分之九,若三塗者,則可阻百分之二十八,對於保持室內溫度之功效,當非淺鮮也。

油池　煤油之類,具揮發性,易於蒸發,經熱漲冷縮之故,儲藏之油,往往生一種呼吸作用,以致日久損失浩大,如能使日光反射,則油池不易受熱,損失自然減少,所以油池或油櫃之外壁,往往以銀色之鋁粉油漆塗之,使陽光反射,不致受熱過分,但銀粉漆之反射與却熱能力,適與事實相反,據隙米脫與威廉兩氏之試驗,白色爲最佳,銀色與紅色次之,卽奈乃生與强姆生兩氏之報告,亦以白

色爲佳。

漆名	煤油損失重量	各漆比較
1. 白漆	397	41
2. 白磁漆	880	91
3. 鋅粉漆	880	91
4. 銀色漆	880	91
5. 黑漆	964	100

據樂司氏與斯太氏之試驗,白漆之中,混以極少之鋁粉,即足以減少許多反射量,白漆如鋅鋇粉,鋅氧粉,白鉛粉,其反射量常在92%之上,若加以百分之一之鋁粉,則落至74%左右,今將其比較列下,以示加入鋁粉之影響:——

加入之鋁粉	鋅鋇粉60	鋅氧粉60	白鉛粉60
%	油質40	油質40	油質40
0	93.5	92.0	92.0
1.0	79.0	74.0	74.6
2.0	69.5	66.5	74.0
5.0	52.5	59.0	58.0

爲謀避熱起見,儲油之池及櫃,均須施用白漆以免許多無形之損失。

假漆概論

(Varnishes)

吳輿生

假漆者何,爲樹脂或油類之溶液,或油與樹脂兼備更加適宜的溶劑之溶液,以之敷於物面,經空氣氧化,能成一種美化的與保護的透明膜層也。其定義雖云如此,但亦非所盡然,有如蟲膠假漆(Shellac Varnish)與酒精假漆(Spirit Varnish)之乾燥,則與養化關係甚少;黑色瀝青(Black Asphaltum)與黑色烘漆(Baking Japan),其護膜並非透明;乾料之加入,亦非作爲護膜。然諸種例外物品,在假漆之製造中,則仍列入之也。審此定義與範圍,故於假漆篇中,可分五項事物討論之。五項者何,原料,製法,檢驗,用處及弊端是也。

今第一所須知之者,爲假漆製自何物?曰樹脂,油類,乾料與溶劑四種是。樹脂之分類,無斬截處。然大別之則有硬質(Fossil),軟質(Non-fossil)及人造(Synthetic)者三種。硬質樹脂可以高列脂(Kauri gum)爲代表,此脂爲一種樹木之分泌物,積壓地下,歷年既久,性乃變硬。大都產於新西蘭等地。先自土中掘出,洗之選之再碎之,依其形式之大小與色澤之均一,別爲門類,售之於市。色淺者價昂且稀,甚少用於製漆中。其他之硬質樹脂,有東印度脂(East India),孔鶴(Congo)及爾松(Gilsonite),上柏(Zanzibar),與泊丁那(Pontianok)等。及爾松爲眞性硬脂,但僅爲黑色假漆或烘漆用。孔鶴質最硬。其餘所謂硬質樹脂者,其性當較硬於軟質也。

軟質樹脂則有台瑪(Damar),瑪介珊(Maccasar),瑪尼拉(manila與蟲膠(Shellac)等。樹脂一章,此時均不詳論,後有專篇敍述,故所

云從略。

人造樹脂之製法,則千方不同,且新法叠出。本節亦不作詳論,惟簡爲紹介者,計分三大品類如下。

最普通者爲甘油硬脂(Ester gum),出源亦由松脂(Rosin)。蓋將松香與甘油在熱與壓力下作用之,則脂化(esterification)作用起。經脂化作用後,原來松脂之性狀乃變成一甘油脂化之樹脂。如以甘油與他種脂類(gum)以代松脂,亦可製得類似之產物。

第二類則爲酚醛結合脂(Phenol formaldehyde resin)。倍克萊脂(Bakelate)即爲其例。阿勃樂(Amberol)亦屬此類。

第三類則爲酯(Alkyd)屬樹脂。甘油與酐之結合物也。

其他之人造樹脂可供常用者爲克瑪六(Cumarone)或茚(Indene)屬。此爲煤膏中之產物。

在製假漆中之第二原料則爲油類。通用者爲亞麻仁油,荳油,蘇子油,桐油,青油,魚油等。礦物油有時亦用之。每種油類,在此如須詳論,費時太多,似有不必。概言之,除鑛物油外,所有油類,其能用於假漆之製造者,均爲天產原料。以此壓榨精製至於各種情況有如色澤,黏度,碘價,酸度等,均達規定之度數,乃爲應用。

第三種原料爲乾料,大都爲金屬之鹽類如鉛錳,鈷,鈣,鋅等。然亦有以氧化物,醋酸化物,氫氧化物爲之者,亦有以金屬皂爲用者。故製假漆者,類能自製之。蓋此等乾料如以金屬與松脂之松脂酸,或林諾立酸(Linoleates)或哪呋唑酸(Naphthenates)乳化,即可生成也。

第四種原料爲溶劑。常用者有松節油,礦物油,燈油,輕煤油(Naphtha)及苯(Benzol),二甲苯(Xylol),酒精等之煤膏中產物。水亦有時用之。

取斯四者,以製假漆只須變其配合成分,改諸操作方法所得種類,可以無限。今暫不論其製造之手續,而僅言其四種原料之配合,可有下列十種組合。

(1) 樹脂與油

(2) 樹脂,油與乾料
(3) 樹脂,乾料與溶劑
(4) 樹脂與溶劑
(5) 樹脂,油,乾料與溶劑
(6) 光油
(7) 油與乾料
(8) 油,乾料與溶劑
(9) 油與溶劑
(10) 皂式乾料與溶劑

至於製造手續,要言之,亦不出乎兩大原理。

一為熱製。用熱來源,可有多端。熱煤,煤氣,油類,電氣與水汀,均可採用。前列三者,為用較廣。電氣不切實用,水汀之熱,容有未足。

在熬漆中次要之具,則為製漆之釜。釜為圓錐形,徑約二呎又半,高約三呎半至四呎半,可以銅或鋁或鎳銅合金(monel)製之。承以矮車,俾便上下於爐竈。釜之裝置,有固定者,亦有活動者。質料除上述者外,亦有以鋼鐵製之。油釜之上,蓋以釜罩,油釜之內,備有溫度計及攪拌器等。

原料與機具備矣,當言煎熬手續。在製含有樹脂之假漆,常以樹脂先熔,如是硬質樹脂,其蒸發程度,須去百之二十。物已變為油類或溶劑可溶性後,乃以油類混入。至於此種樹脂之蒸溜溫度,恆為華氏600與650度間,然溫度與時間,亦不能每次類同,因天產樹脂,卽使係一上品,而其成分與性質亦多出入。以故,吾人不能言百磅之高列(Kauri)在兩刻鐘內於610°F上必能全體熔好,是以經驗尚矣。故熬油之人,當手執一棒,試入熔脂之中,然後拖出察其流動之性質,抑或滴落熔脂於玻璃片上,以覘察之,蓋已經熔好之樹脂,自棒上落下之情形,與夫棒上所有泡沫之數量,均能訴其煎熬之程度,而決其能否溶於油中或溶劑中也。樹脂煎畢,釜卽離火,油乃注入釜中。油類用亞麻仁油或桐油,生熟均宜,亞麻仁油與桐油

參用亦可。加油溫度,固宜較熱,然冷時亦良,此端惟恃吾人如何運用耳。油既入釜,拌和再熱,直至油脂兩物體貼化合然後止。油釜離爐,則加乾料,繼拌於適當之溫度間,大約爲500°F左右,待乾料盡爲假漆所吸取,乃置一點於玻版之上,能呈透明狀態者爲佳。於是置之使冷,移入他室,溫度降近 450° F時,更以溶劑攪入。松節油,礦油燈油,均可合用,惟在此溫度時,松香水(Naphtha)或煤膏溶劑則不能加入,須有待於再低之溫度也。以上所述,爲製造假漆之一般程序,卽係用樹脂,油,乾料與溶劑四種成分之製造法也。

至於其他之假漆,如以油與樹脂製成者,則先熬油,後以樹脂熔入之,有時亦以兩物同熬。至於樹脂與乾料所配成之假漆,係以乾料先熔於油中,而後再加樹脂。此兩方法,在製印墨法中幾盡採用之。

最廉價之假漆,大率爲光油(Gloss oil)或天花板假漆等。此等假漆係以松脂,乾料,溶劑三者混合之。蓋以松脂先熔,加熱至500°F,則加石灰硬化,待已全體化合,再以溶劑稀薄之。

在以樹脂與溶劑所製之假漆,則恆用台瑪(Damar)與一部之溶劑先行溶解,然後稀以餘量。

以上所言,爲以硬質樹脂,油類,乾料,及溶劑所製之假漆。如以軟質樹脂代用,則手續頗有不同。用甘油硬脂(Ester gum)時,溫度即不必如此之高。用硬質樹脂時,其溶解實爲首要。用甘油硬脂爲桐油假漆時,則以油之煎熬爲要著。常法係以一部之樹脂與油合煎,溫度升至525°-560°F間,有時可以略高,直至油質變厚,或領起時能成線形,於是加其餘量之硬脂,有時更可加以若干之亞麻仁油與乾料再行煎熬,及至適度,始行離火待冷,再加溶劑稀薄之。

如用他種人造樹脂,則恆以樹脂與油入釜同煎,其溫度當猶低於甘油硬脂者。

熱製假漆外,更有採用冷製者,則爲蟲膠與酒精假漆之類是也。法以樹脂與溶劑體貼混和便可。

假漆製就,則當轉送,過濾,收藏,並檢驗之。轉送藉管子,邦浦及重心之利用;過濾用離心機或壓力機;收藏用木製或鋼質之桶,形圓形方,依利選擇。

檢驗一事爲第三要的。蓋製假漆時所試用各種配合手續,如欲求得美滿之產物,廠中自當細加檢驗,使其出品不致流於標準以下也。在轉送之時,卽須檢驗其黏度與色澤。法以瘦小長筒一枚,盛以所製之假漆與二號之標準相比較,所謂二號之標準者,是此物已與標準器作過測量者也。黏度之標準器是用 Gardner-Holdt 管,色澤之標準,則用旋轉之比色盤。在過濾室內,亦須複驗其厚薄,色澤及其清晰度。濾後入桶,複驗完畢,始備供用。

所謂複驗者,除檢驗其厚薄,色澤與清晰外,並須測定其每介之重,不揮發物量,初凝性 (Setting) 乾燥性,結硬性與夫光澤,冷熱水之抗力,酸價,穿氣試驗,加脂試驗 (Kauri reduction test)與曝露試驗等項。諸種檢驗,如欲一一詳加說明,似無需要,可於他章專篇列論,茲僅擇一二事項,略以闡明其關係足矣。

以假漆爲製漆或磁漆之液劑(vehicles)者,其酸度之測定至關重要。酸度測定後,則加相當之鹼以中和之。蓋液劑有酸,而採用鉛粉或鋅白爲顏料時,則此酸可以興起皂漿狀 (livering) 作用,或使漆質增厚。皂漿狀作用固不盡由酸度起,然酸度必爲其主因之一,則無可諱論。

以桐油製造假漆與磁漆時,穿氣試驗實有特別之意義。用油煎熬不確,氣候又屬不正,則漆膜乾燥,常自紋裂,此使製漆者有絕大之驚異。因斯常須特法以免其弊,且於每釜產品,均須試過,用知其性質是否適合,並須試得,卽使置於特別情況之下亦得應用無疵。

加脂 (Kauri reduction test) 試驗爲檢驗假漆所含油量 (oil length) 及其彈性者也。然同時其對於抗水性質之試驗,均足以表示假漆磨損力之優劣。惟近今所宜注意者,卽加脂試驗實有不能確

切代表之處,因假漆之製造可自酚醛樹脂或甘油酐樹脂者,則其結果無由表獻矣。

烘漆(Baking Varnish)之應用在於高熱,故須用高溫試驗。物品漆須用磨擦試驗。漆與磁漆之液劑,須有實際之研磨以知其變厚情況,流動速度,粉刷難易,光度(gloss)保存以及色澤變易。總之每種假漆均有其相當之試驗,使化驗間之工作,恆在緊張情況也。

原料,製法,檢驗均已述一梗概矣,茲當以其各種代表假漆,依其目的或其用處,約略申述,用以闡明實際情況,亦屬要圖。

地板假漆　假漆之用以塗地板者,性質當極度堅硬,且常須有高度之光亮,遇冷水或熱水,不變白色,遭猛力之磨損,亦無白痕。是以硬度一端,務必牢記于衷。普通用油廿四介,配以樹脂百磅,一再煎熬,耗損迨餘十六介時,跡近完工。不揮發物至少當含百之五十。用油以桐油爲宜。

配　方

(a)	桐油	36 介
	亞麻仁油	4 介
	硬質松脂 No.1	40 磅
(b)	硬質松脂 No.1	60 磅
	密度僧	8 磅
	紅丹	4 磅
(c)	輕煤油 54°	72 介
		121 介
	損失	7

每介重7.25磅,產量114 介

40 磅之松脂熔入混合油中,先在 540° F 煎熬之,然後離火,溫度約能升至 580°F 或 590°F,但不得過 595°F。溫度降至 580°F 時,以 60 磅之餘量松脂攪入,以至熔盡,溫度約須降至 500°F。於是重上爐竈,煎熬至520°F,再行離火(熱度能升達 540—550°F)。溫度開始下降,即以乾料散入,繼續攪和,闢去油沫。冷達330°F時稀以輕煤油。

硬質松脂 No.1 之配製

中色松脂	100磅
風化石灰	5磅
	105磅
損失	15磅
產量	90磅

熔松脂達500°F,舉釜離火,乃以石灰散入,不絕攪拌,上浮泡沫,則去之。反爐再熱至575°F,復離火爐,漸冷達480°F,乃傾入冷箱中。

室內裝飾假漆 此漆包括種類甚多。光油 (gloss oil), 硬油 (hard oil),傢俱漆 (furniture varnish), 室內漆 (interior spar) 等均是也。然諸種假漆均可出自一釜之中。光油者無他,僅松香石灰與稀薄劑耳;硬油與光油同,惟質較優,百磅樹脂,含油二十至十五介也;甲乙兩種傢俱假漆,則列於光油與硬油之間;室內漆,有冷水抗力性,每百磅樹脂配油十五介至廿五介。無光假漆(Flat varnish)爲室內用,此漆之製造最感困難,因使用者,各具意見,各懷標準,各欲得一如何方合已意也。此種假漆恆以東印度樹脂製之。然以普通之假漆加以無光劑如脂酸鋁 (aluminum stearate) 者亦得之。磨擦假漆 (rubbing varnish) 爲漆木器用,用油量少,樹脂用孔鶴 (Congo) 或高列 (Kauri) 之屬。

光油之製造

F 松脂	300磅
風化石灰	9磅
輕煤油(54°)(Naphtha)	24介

54介 損失4介 產量50介

以松脂先熔,煎熬達500° F, 舉釜離爐,乃以石灰散入,力拌使和,面沫可撂去之。待石灰已被吸盡,泡沫亦已漸息,反釜爐上,加溫至560°F。離火後,冷却至320°F,乃以輕煤油稀薄之。初加宜漸,繼以拌和,後再下降,乃以大量加入。

無光假漆之製造

(a)	脂酸鋁	20磅		
	松節油(Wood turpentine)	10介		
	松節油	30介		
		42½介	損失2½	產量40介
(b)	脂膠 (卽(a))	10介		
	松節油	10介		
	假漆No.2	20介		
	松節油	15介		
		69介		

(a) 以20磅脂酸鋁入10磅之松節油中,用隔層水汀熔解。再與松節油冷和,後加熱至140° F,在此溫度中繼續攪拌待成膠狀,溫度切勿過180°F,於是過夜待冷。

(b) 以10介之脂膠 (a) 和20介之松節油後,乃注入假漆No.2中。脂膠入假漆,能使凝固,故須不斷攪動,然後靜止五小時,再以15介之松節油稀薄之,或規定其量,以求所定光度,然後以布濾過。

假漆No.2之配製

桐油	45介		
硫酸錳	4磅		
硬松脂	100磅		
亞麻仁油	6介		
輕煤油	48介		
濃乾料	1介		
	110介	損失5介	產量105介

以松香入桐油在320°F熔解之,以硫酸錳散入攪和。待硫酸錳已經熔完,加熱至565°F,乃離火。熱升至580°F時,卽以6介之冷亞麻仁油注入,拌和兩三分鐘,溫度可降至460°F,目的是不使煎熬過度也。在460°時加輕煤油,然後成乾料。但須攪拌均一爲要。

硬松脂之製法

松脂	100磅

風化石灰	7 磅
林諾立酸鉛	5/8 磅
林諾立酸錳	1/8 磅
甘油	2 磅
	109 $\frac{3}{4}$磅　損失4 $\frac{3}{4}$磅　產量105磅

熔松脂於500°F,加石灰,加熱至575°F。冷至500°F 加鉛錳化合物,拌和以待溶盡,加甘油再拌。

濃乾料之製法

亞麻仁油	50 介
紅丹	100 磅
硬松脂	100 磅
二氧化錳	75 磅
松節油	100 介
輕煤油 54°	100 介
	261 介　損失15介　產量246介

先以40介油熱至420°F,乃以紅丹徐徐加入留在油面約兩三分鐘,然後拌之。在420—480°F間煎熬之,續拌不已,有沫可以撂去,約半小時紅丹被吸入,乃加松脂,攪之使熔。松脂熔後,溫度尙在420°F,乃加二氧化錳。加亦不宜快更須不斷攪拌。二氧化錳加入迨半,則以餘油10介注入,復熱至420° F,再加餘錳。煎熬於426—480°F間,待錳熔盡,色呈琥珀,共須時約二句鐘。至性脆硬不黏時,煎熬終了,於是冷却至450°F或420°F以松節油稀薄之,溫度降至320°F,則入輕煤油。

硬質假漆 (Spar Varnish)　爲戶外用,每百磅樹脂至少用油三十三介。用桐油時,甘油硬脂(Ester gum)爲適用之樹脂。亞麻仁油與桐油合用時,高列(Kauri)樹脂沿用之。阿勃樂(Amberol)或倍克萊(Bakelite)亦可與桐油合用。

普通硬質假漆之製造

淺色甘油硬脂	100 磅
桐油	32 介

乾性桐油 No.3	4 介
重質輕煤油 48°	80 介
濃乾料（見上）	1 介

127 介　損失 5 介　產量 122 介

以甘油硬脂熔於桐油中,快熱至520°F,釜卽離爐,溫度仍升,達565°F,但不過575°F。不斷攪拌,溫度漸降至565°F時,卽以四介之乾性桐油加入之。拌和,降冷至450°F,加輕煤油及乾料。

乾性桐油之製備

桐油	45 介
亞麻仁油	5 介
密度僧	8 磅

50 介　損失 2 介　產量 48 介

兩油相台,迅熱至420°F,最高達448°F,待降低有五度時,則加密度僧兩磅,任浮油面兩分鐘,然後拌和至其全體熔入,在加完之前溫度仍須在440°F以上。復熱達450°F歷半小時,或待乾料全體熔解爲度,然後離火使冷。

傢俱假漆(Rubbing Varnish)及推光假漆(Poilshing Varnish)兩種,每百磅樹脂配以十二至十五介之油類,樹脂常用硬性或半硬性者如高列(Kauri)孔鶴(Congo)瑪尼拉(Manila)等。

推光假漆製造法

WW 松脂	100 磅
風化石灰	6 磅
醋酸鉛粉末	8 磅
硼酸錳	2 磅
桐油	16 介
松節油	8 介
輕煤油 54°	32 介

66 介　損失 4 介　產量 62 介

置松脂於釜底,上敷石灰,以錳鉛兩物混和置於石灰面層中部,熱在400°F前無沫溢出,不必攪動。400°F後,不斷攪動,熱徐升,達550°F,釜乃離火,卽以冷桐油注入。繼拌,復熱達520°F,離爐仍能繼升至565°F,但不過575°F。於是使

冷至 420°F 時加松節油,300°F 加輕煤油。

磨擦假漆之製造

(一)

甘油硬脂	90 磅
樹脂鉛(lead resinate)(末)	9 磅
樹脂錳(末)	1 磅
桐油	10 介
松節油	10 介
輕煤油 48°	20 介

50 介　損失 2 介　產量 48 介

熔硬脂於桐油,速熱達550°F,離爐後升至 565°F,但不過565°F。加鉛錳兩物,拌和使熔,至 425°F時加松節油,繼以輕煤油。

(二)

淺色瑪尼拉	85 磅
W.W.松脂	15 磅
風化石灰	2½ 磅
亞麻仁油	35 介
密度僧	2½ 磅
松節油	40 介
輕煤油 48°	14 介

95 介　損失5 介　產量 90 介

以瑪尼拉脂入釜,上蓋,熱至620°F,待成液體,乃去火五分鐘。啓蓋,重熱至550°F 與 650°F間,至拌之能如油狀,須時約一時至一時半。去火後即加松脂,全熔後,則散石灰,攪和。上蓋急熱至 550°F 復離火,加熱亞麻仁油 (450°F) 如線狀。加畢,再啓蓋,加熱至 480°F,持此溫度煎熬達四小時,或至已達適度爲止,乃去火加密度僧。拌之使冷,在 440° 時加松節油,繼以輕煤油。

(三)

淺色孔鶴	150磅
M.松脂	30磅
桐油	13介

燈油 46°	$2\frac{1}{2}$介
醋酸鉛（粉末）	$4\frac{1}{2}$磅
松節油	14介
輕煤油 48°	20介

$67\frac{1}{2}$介　損失$4\frac{1}{2}$介　產量63介

以樹脂在釜中熔解達625°F,離爐待冷。至550°F時乃重熱至625°F,復冷至550°F,於是上蓋加熱,在625°F時持兩分鐘,乃離爐加桐油10介如綫狀,惟此油須先熱至300°F。拌和後去蓋冷至525°F時再加桐油三介拌和之。

再熱至550°F離火冷却至525°F,散入醋酸鉛每次加量須少,以防泡沫溢出釜外。乾料加完,泡沫亦止,再熱達540°F。離火冷却至500°F時,則以溶劑攙入之。

烘光假漆(baking Varnish)　製法甚多,因目的不同而異其配合。普通樹脂百磅,用油不逾三十介,除非有特別應用處,油量亦可加增。

烘光假漆之製造

石灰松脂	100磅
錳粉(Mno_2)	2磅
桐油	36介
乾性桐油（見上）	4介
密度僧	8磅
燈油（Kerosene 46°）	36介
輕煤油 54°	36介

122介　損失5介　產量117介

熔松脂於桐油至350°F,以錳粉散入,每半磅一次,攪和,在半小時內,溫度可升至480°F,再溫度徐徐升至此點時,即遽熱達565°F乃離火。待溫度已達590°F時,急以4介冷乾性桐油注入,攪和之。溫度降至565°F,即以密度僧散入,一磅一次,浮留油面達三十秒,然後加拌,惟須在500°F前加入。冷至450°F,乃加燈油;300° F時加輕煤油。

石灰松脂係以100磅M松脂6磅風化石灰熱至575°F製成。

黑色假漆(black finishing)　有在空氣中乾燥者與烘乾者兩

種,及有含顏料,不含顏料者之別。通常厚料爲及爾松 (gilsonite) 地瀝青 (pitch) 與亞麻仁油。魚油,以及適合之溶劑,亦常用之。

普通黑漆（烘乾）假漆

及爾松 No.2	200磅
錳粉	2½磅
亞麻仁油	9介
夏黑油(Summer black oil)	3介
燈油46°	13介
輕煤油54°	25介

70介　損失4介　產量66介

以及爾松入釜底上注亞麻仁油,面敷錳粉。加熱約達 300°F,全體變爲液狀時,入溫度計,再升熱至 450°F 不斷攪和之。在 450—460°F 煎熬兩小時,再升至 480°F 歷一小時或至不含塊狀。離火。加夏黑油,拌和,重熱徐升至500°F 後,繼拌使冷。達480°F 時加燈油,300°F 加輕煤油。

用時須烘至 300°F 歷二小時或 350°F 歷一小時。

優等黑色假漆

亞麻仁油	50介
褐石(burnt umber)	25磅
瀝青(Barbadoes asphaltum)	150磅
高列漆	25介
燈油	45介
松油(pine oil)	12½介

置褐石於油中,加熱達450°F—500°F歷五小時。另以瀝青熔解,然後注入油中,煎熬達兩小時,持溫度於 400°F。先以高列漆稀薄,然後加以燈油繼及松油。

高列漆之製備

高列粉	100磅
松脂	24磅
錳油	8介
燈油46°F	16介
松節油	8介

以高列先熔,去蓋加松脂。加油熱至480°F,持此溫度熬三十分鐘。離火加燈油。300°F時加松節油。錳油為59介亞麻仁油與39磅之錳粉煎至600°F而成。

乾料(driers)　如松脂,乾料,溶劑混合一體者為之棧乾料(brown japan)價廉。另有以硬質與油混合或與磨乾料(grinding japan)混合者。磨乾料為蟲膠,油乾料與松節油配成之。

樓乾料之配製

松脂	100磅
風化石灰	5磅
錳粉	$2\frac{1}{2}$磅
密度僧	3磅
磨光油	2介
重輕煤油48°	9介
輕輕煤油54°	21介

熔松脂,上蓋以石灰,錳粉與密度僧。溫度計至480°F煎熬半句鐘,或待石灰已為松脂吸收後,加磨光油2介。拌和加熱至480°F,熬十分鐘,離火加重輕煤油,冷至300°F加輕輕煤油。

磨光油係以80介亞麻仁油 $1\frac{7}{4}$ 磅之密度僧 $4\frac{3}{4}$ 磅之硼酸錳在520°F時六小時熬成之。

磨乾料(Grainding Japan)之配製

亞麻仁油	50介
錳粉	20磅
紅丹	80磅
漆蟲	48磅
密度僧	20磅
松節油	64介
重輕煤油48°F	56介

以油熱至240°F,加紅丹,每五磅一次,拌和。紅丹加了,升熱至420°F。續拌不已,待無泡沫,再升熱至450°F但不過480°F。熬三十分鐘,以使紅丹全部被吸。離火,加錳粉半磅一次,易起泡沫,故須拌和不已。在300°上錳粉須加完,復熱至420°F—450°F歷十五分鐘,泡沫不再起時,乃加蟲膠以每小片加入之併以

攪動。加畢,復熱至 420°F 歷 30 分鐘。最後熱至 450° 歷五分鐘,乃離火而稀薄之。

至於油漆與磁漆之液劑(Vehicles) 則有各種不同之特品。多油磁漆液劑'(long oil enamel vehicle) 與磨光液 (mill gloss liquid) 常爲油,乾料,與溶劑用適合之處理方法以得極度之光亮與色澤者是也。其他之磁漆劑,可以松脂,甘油硬脂(ester gum)台瑪 (Dammar) 或阿勃樂(Amberol)與油,乾料及稀薄劑製之。四小時乾燥液劑(four hours vehicles) 常以人造樹脂製成。上等無光漆劑則含多量之油與多量之不揮發物。其他之特品如交通用具漆液劑及鋁漆液劑等,應在釜中留心煎熬,使得一善流易刷之良品焉。

四小時乾燥假漆之配製

桐油	21介
25% 阿勃樂(Amberol)	100磅
熱至 500°E 時,加密度僧	3磅

熱持 550°F 歷二十分鐘加熟亞麻仁油 (3 hrs. bodied linseed oil)4 介樹脂錳 2 磅。熱至 530°F 時離火。冷後加二甲苯 10 介,輕煤油 25 介。

以上所言類屬製造方面,至於銷售情形,則大半買客對於乾燥一端,最易發生枝節。如有此遇,第一當問其天氣如何,因氣候之乾濕,最有影響;其二爲被漆面層是否含有油水之物,第一層漆膜尚未乾燥,而續行再漆,亦有此弊。

膜層之易被磨損者,亦爲常有之困難。然此事有百之九五由於假漆之不善,然亦能因底層有弊而起。如假漆中用有蟲膠代用物,以及價廉之木質塡充物者,常遇此患,然如先以此漆試敷於玻片上,待乾試括,苟無所損,則應用於木器之上,必亦完善矣。

水花(Blooming) 不常遇,如有,則定係油類煎熬不善,有時以醋與水洗之,能救此患焉。

註:本篇是取材於 Paint and Varnish Lecture Caurse 及 Scott: Formulary 兩書。

造漆之配色問題

韋鏡權

漆料之配色,通常可用數種方式,以配成某種指定之色彩。如於顏料中,加以選擇,不但可得所需之色調,尙可使配成之顏色,具有必要之特性,故配色中有種種之問題,頗值討論也。

凡無機性顏色,無論單純用之,或與他種顏色混和用之,所製成之漆料,均能耐光持久。而多數之有機性顏色,在單純用之時,尙能持久,若爲着色而用,則一與他種顏料或粉料混和,所配成之漆,多不能持久。是因有機性之顏色,無論加以何性之顏色,其耐久性均大被減削。有本屬耐久性之有機性顏色,一經和以少量無機或有機性,又有同等耐久性之顏色,則所成之漆料,於暴露風日之後,其由有機性顏色賦予之色彩,必日久而稍褪。故概括言之,凡用於露天之漆料,宜用無機性顏色以配色,如用有機性之顏色,則必選其耐久性素著者而用之,尤不宜用少量而與他種顏色合用,否則即最能持久之顏色,其壽命亦未有不縮短者。

在褪色試驗器中,漆料之色彩,能變成各種色調,如加以嚴密之考察,并輔以下列各條之檢試方法,則其變色之程序,及其色彩之由何種顏色配成,頗不難明確推斷之。

黃色——油漆磁漆或噴漆,無論其爲何種漆料,取少許塗抹於白紙上,而以硫化鈉溶液試之,如現黑色,可認爲係用鉻黃(Chrome yellow)配成。但漆料中用含鉛之乾燥劑(dryer)太多者,亦有相似之結果,不可誤認。鉻黃不溶於醋酸,而溶於鹽酸,又曝於日光中

即逐漸變黑,頗足資爲旁證。鋅黃(Zinc yellow)遇硫化物不變黑,曝於褪色機中。亦不現黑色,但溶於醋酸中。Hansa yellow 曝光不發黑,遇濃度20%之NaOH,亦無變化,但遇哥羅仿($CHCl_3$),則易溶而走色(Bleeding)特甚。鎘黃 (Cadmium yellow) 能耐鹼,一遇鹽酸,即放出硫化氫而失去色彩。

綠色——鉻綠(Chrome green)係鉻黃與鐵青(Iron blue)配成,後者易爲鹼所侵溶,故鉻綠亦易爲鹼所侵溶;又因含有鉻黃之故,亦易與硫化鈉起作用。氧化鉻(Chromium oxides)有特異之色調,大不如鉻綠之明麗,鹽基性氧化鉻 (Hydrated chromium oxide) 則特別鮮明,此二種綠色顏料,最能耐光持久,無論何種液料(Vehicle)與溶劑,其色均不溶化而走色,無論酸鹼,均不發生變化。有機性之綠色,其色彩恆異常鮮明,但於褪色試驗機中,其色不能持久。大多數之有機性綠色,遇酒精即溶化而走色。

藍色——鐵藍耐光持久,耐酸而畏鹼。羣青(Ultramarine blue)則反之,耐鹼而不耐酸,遇鹽酸則放出硫化氫而藍色消失。漆料中含有硫化鋅或Lithopone。亦能發生此氣味,故有時須取樣品少許,以火煆之,煆後仍能保持藍色者,必爲羣青(Genuine cobalt blue價值昂貴,未必用於油漆中,)。如煆後無藍色存在,則其藍色必爲有機性藍色與Lithopone混合而成,凡屬有機性藍色,必於褪色試驗機中褪敗,又於遇火酒時,其藍色大都浸聚於邊際。

紅色——因有機性紅色顏料甚多之故,紅色顏料之檢定,較爲繁複。所幸各屬各系之紅色顏料,各有其特別之色彩,可與已知者比較而確斷之;又可視察其遇硫酸或燒鹼時,所生之色彩而判定之;又彼等之耐光性,差異懸殊,亦可資爲佐證焉。Toluidine red系之紅色,遇醇溶KOH時,無藍色現出,其未攙和他種顏料者,耐光性頗强,能全溶於哥羅仿 ($CHCl_3$) 中。Para red有特異之色彩,遇醇溶KOH,則現藍色,遇油則浸集於邊際殊甚。Lithol red系之色彩光鮮,遇醇溶KOH不變色又能耐熱,遇溶劑亦不浸集於邊際,但不及前

二系之耐光而已。顏料在漆料中,常因有液料將其包圍掩護,不易檢試,須用溶劑溶去液料,而以留下之顏料供檢試,則其結果,乃能正確。

在配色時,如覺有攙和白色不透明顏料之必要,則須切記所謂白色之顏料,無一眞爲白色者。每用同一顏料,與各種之白色顏料配和,而所成之色調,每差異特甚,至爲可驚。蓋自配色之觀點論之,世固無絕對之白色顏料也。

漆料髹塗後顏色耐久之問題

漆料一經髹塗,暴露風日,顏色卽褪敗,其理由可略述如下:

(1)　眞確性之褪敗。

(2)　與折光率變化之關係。

(3)　脫蝕剝落。

(4)　新物質之生出。

(5)　顏色之分解。

(6)　由尙未明晰之原因,所引起之色彩變化。

所謂眞確性之顏色褪敗,乃日光所引起之結果,但漆料中常用之無機性顏料,則無發生此種眞性褪敗之可能,例如鉻黃與鉻綠,亦不過發黑而已。有機性顏料則不然,如 Hansa yellows 及 Toluidine, Para 及 Alizarine 各系之紅色,僅於不與他種顏色相和時,能耐光持久而已。此外漆料中之惰料,對於色彩之耐久性,常有重大影響,因漆料中之油或其他液料,一經分解,而折光率即隨之改變,故油料之色彩,受其影響亦鉅。再則顏料與各種惰料之體積之比,所關於色彩者亦大,因各種惰料之比重不同,而配料時,則以重量爲根據,是以顏料與惰料之體積之比率,變化亦大,影響於色彩之濃淡者亦多。

罐中漆料保持色彩之問題

近年人多用有機顏料,以配成鮮明之綠色或藍色漆料,不求其能充分耐光持久,再則因使用人造樹脂以製造漆料之故,此問

題遂趨於複雜。爲使漆料之色彩,在罐中能久保,及髹塗後能持久耐光計,自宜用鹽基性氧化鉻與鉻黃攙配,以製成各種深淺之藍色綠色漆料。若耐光性不爲必需者,亦可用磷鎢酸鹽與有機顏色結成phospho-tungstic lakes而用之。凡漆料若用鹼性之顏料,如氧化鋅,碳酸鉛,及其他之鹼性惰料,或用鹼性溶液於油料中,則漆料之色,在罐中均不能長保不變。

防止漆料浮離之問題

製成之漆料,其顏料有時儼然各分爲一層,其原因雖不全知,但與顏料對於液料之濡潤性有關,可無疑問。雖無簡單之補救方法,但於加工研磨,多加惰料,增減液料之酸度,或加入金屬皂諸法,用其一或兼用之,總能有補救之效。

防止漆料在罐中沈澱之問題

除爲防止浮離漫浸外,於漆料中加入惰料,實屬無謂,蓋增厚漆料之實體,尙有其他方法可用故也。磁土有優良之浮懸性,如有必要時,亦可用白石粉(Whiting)及與鹼類無作用之顏料代之,但於用鉻綠作顏料者,不可用之。

顏色走色(漫浮集邊)之問題

無機性顏色,無論用何種液料配成之漆料,均無顏色漫溶及集聚於邊際之象,有機性顏色則間有此現象所以須分別加以注意。其唯一之安全辦法,爲先將應用之液料與顏料,混合而試之。含Toluidine red之漆料,如於其上塗以白色漆料而烘烤之,則紅色必漫浮於白色之上,若於空氣中,任其自乾,則可避免此惡果。各種紅色顏料中,以Lithol reds爲最不易有走色之弊者但亦以不與煤膏溶劑相和用爲限。

對於熱之抵抗問題

液料之本身,必須於烘烤磁漆之溫度,能不起色彩上之變化,爲此問題中首要之點。至於烘烤磁漆時間之長短,較之烘烤溫度之高低,亦屬較爲重要,因若干色彩,能耐短時間之高溫,而不耐長

時間之低溫故也。

〔附註〕本文原文標題爲 Problems involved in the formulation of protective coatings form pigment colors, 係 A. F. Brown 所作,載於 Paint and Varnish Production Manager, February1936,抉要譯述之如上。

鋅面與油漆層間之反應

韋鏡權

塗於白鐵表面之油漆,日久即不能黏着而脫落,其原因雖可作種種之想像,但其中之可能者,則爲油漆變乾時,有由分解而成之物,與鋅起作用,於油漆層與鋅之夾層間,產生新物質,使二者不能黏貼是也。

油漆層自白鐵上剝落時,若係面積大者,其與鋅接觸之一面,常若有白色之薄層,附於其上,固爲習見之事。特鋅與油漆膜之間,究能有其他之化合物存在否,此種意見,正有待於研究也。

此項研究,可分爲二部份:其一則證明油漆於變乾時,確有由氧化而生之物,與鋅起作用;其二則此種作用所生之物,已於自白鐵剝下之油漆層上,證實其存在,而蟻酸鋅(Zinc formate)之存於其中,尤爲正確無誤。

爲便於觀察微妙之作用,及易於取得產物計,將鋅於高度眞空中蒸餾,使塗附於玻璃上,成爲鋅鏡,以資應用。次則於明角(cellophane) 之二面,各塗以由桐油製成之油漆於其乾後,割裂成條,蟠繞於一直徑十公分 (10cm) 之結晶皿中,以供實驗。油漆於變乾時,所放出之酸,其作用何如,亦即用此以作觀察。此後將鋅鏡置於結晶皿之中央,鋅面向上,另取一直徑爲十二公分半之結晶皿,將前皿置於其正中,兩皿間之空隙,注入蒸餾水,深達一公分半,乃以大玻璃片,蓋覆其全面。此整套之裝置,即移入 40°C 之常溫槽中,以待變化之發展。油漆膜既曝露於潮濕之氣氛中,溫度亦升高,氧化與

分解,自必加速進展,只兩小時中,鋅鏡上之鋅,即漸起變化而消失不及廿四小時,鋅已完全不見,只有白色之物留存於玻璃上,是爲蟻酸鋅,其反應業經明確檢定。

次則於鋅片之表面,塗施油漆,剝取油漆膜,以作實驗,亦可由重鉻酸鉀 ($K_2Cr_2O_7$) 之反應,以證實蟻酸鋅之存在。又於白鐵及鐵之表面剝下油漆膜,以供檢試;則白鐵上之油鋅層,其附着於鋅之一面,有蟻酸鋅之反應,而他一面則無之;自黑鐵片剝得之油漆層其兩面皆無蟻酸鋅之反應,殊足爲顯明之對照。

〔註〕本篇原文載於J. Industrial & Engineering chemistry, February 1936; 作者係Henry J. Wing, Antioch Industrial Research Institute, Yellow Spring, Ohio, 標題係Reaction Between Paint Films and Zinc Surface., 茲僅摘譯其要旨。

桐油油膜發生晶紋之原因

韋鏡權

凡含有桐油之油漆,其油膜乾後,顯出晶紋,實導因於其周圍之空氣中,含有二氧化氮(NO$_2$)之故。若用百分之八十之氬,與百分之二十之氧,混和而成氣體,以代替空氣,則其中加入之二氧化氮,若僅千萬分之三,亦不足以使油膜發生晶紋,必須增至千萬分之四,乃能有晶紋出現,此則本文作者研究而得之結果也。

此項研究所用之儀器,有一鐘罩形之玻璃罩,其中幷有挾持油漆板之架,又有燃燒氧化乙稀(Ethylene oxide)之尖管頭,又有發生電火花之火星塞,以及排氣裝置,及導入氬(80%)氧(20%)混合氣之裝置,及氣壓表等。

實驗之舉行,可分爲數段。先於玻璃罩中,用通常之空氣,次則改用氬與氧之混合氣體。其結果則用空氣者,無論燃火焰或用電火花,俱能使油膜發生晶紋;而在氬氧之混合氣中則非用電火花,不能使油膜發生晶紋;因火焰之溫度不高,不足以使氬中所夾雜之極微少之氮,與氮化合而成二氧化氮故也。

又於供實驗用之氣氛中,加入二氧化氮,其量須隨人意以增減,所得之結果,爲二氧化氮之量,雖少至千萬分之四,亦足以使油膜發出晶紋云云。

〔註〕原文係 Julius Hyman & Theodore Greenfield 二人所作載於 J. Industrial & Engineering Chemistry, February, 1936. 標題係 Cause of Crystallization of Tung Oil Vehicles, 茲譯其重要之點如上。

哪呋呏酸乾料

吳興生

哪呋呏酸之金屬鹽用爲油漆中之乾燥劑者,已非新奇之產物。如喃呋呏酸錳與鉛,在廿五年前已有其應用哪呋呏酸銅,早已應用爲木料之防腐劑名曰克不侖諾爾(Kuprenol)。以前市售乾料,是否已爲精煉物品,一若現在之哪呋呏酸鹽者,固不得知,但大概已爲改進之品質,非若祕製乾料(Patent Drier)矣。

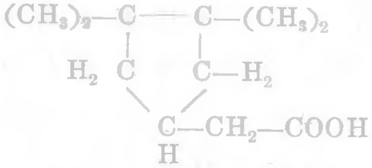
自油漆製造之發展依科學爲根據後,他種工業亦隨之而起更求精進,如哪呋呏酸原料一物充爲乾料時,質地須求純粹,而使出品之成分不致有極大之上下。

至於吾人所欲求得之理想乾料,今日仍在意測之中,哪呋呏酸尙非盡善,惟此項新式鹽類,業已得有重要之地位在此黑暗之境界中,實已展開一新的研究途徑。

哪呋呏酸(Naphthenic Acids)

哪呋呏酸大都產於石油中,今日市售諸品,皆來自羅馬尼亞(Roumania)或俄國油中。在美國之原油中亦有之蓋在英國市場中,已有美國哪呋呏酸,爲其明證。

哪呋呏酸爲一種碳醯酸(Carboxylic acid)且大都是環己烷(Cyclopentane)之衍生物,公式爲 $C_n H_{2n-2} O_2$



如上所寫構造式之物質已可分離得之,但市上之哪呋吐酸,尙爲幾種酸類之混合物。

在英國市上之商品,爲淺櫻色,比重爲0.98 酸價爲250。其酸價之高低,可依需求情形而得之,下列兩端,尤當注意:

(一此物之所以能得極度安定者,實因其性質飽和與含有五個數字環狀物之故。

(二)在今日最高標準之化工分溜法中,已能使此物於石油分溜時得有明確與極精之提煉,幷得有一定之酸度。因之,乾料製造者亦能製出一金屬量無分上下之皂化物。

哪呋吐酸乾料之製造

此種乾料之製造,他處已有詳細之著述,今則略述其梗概足矣。製法係先以是酸用苛性鈉溶液中和之,然後以金屬鹽溶於水中而加入,待至再無沈澱生出時爲止。如以錳鹽爲代表作用,則化學反應有如下式:

$$2\,RCOONa + MnSO_4 \longrightarrow Na_2SO_4 + \begin{matrix} RCOO \\ RCOO \end{matrix} > Mn$$

上層硫酸鈉清液傾去之,下層沉澱洗濯之,待無無機鹽類存在爲止,加熱燒乾。有時置於空氣中待乾,呈碎裂狀。在美國,尙有製出時卽溶於有機溶劑如二甲苯 (Xylol) 呈溶液狀態者。據云以此法處理,可將其中所含水份離析之。

如此物之酸價爲 250—260 卽其平均分子量爲215時,從簡單算法卽可算得鈷鹽約含百之十二半,鉛鹽含百之三十三與錳鹽含百之十一。此種乾料在市上約有四種形狀:第一爲固體,含有極多量之金屬根有如上述者,或更爲普通者,則有複性金屬如鉛鈷,

鉛錳,鈷錳,或鉛鈷錳一同存在,第二種則與亞麻仁油作一濃液狀態或瀰散狀態者;第三種爲瀰散於有機溶劑中如苯(benzol)或二甲苯之類者;第四種則呈漿糊狀。

優良乾料之品性

優良乾料,須具下列特性:

(1)有高量之有效金屬,故有極强之乾燥性。

(2)有安定性。

(3)有極大之溶解度或極易瀰散。

(4)性中和。

(5)對於漆膜無損壞之患。

於今乃論各種乾料之性質,如以熔解法(fused method)或沉澱法所製出之樹脂酸乾料(resinate drier),林諾立酸乾料(linoleate drier)與哪呋唑酸乾料(naphthenate drier)等一一論之,似多裨益。依經過所知各種金屬化成之乾燥劑無論爲爲何類其效用,均屬無甚差別,卽林諾立酸,樹脂酸或哪呋唑酸所成之鈷乾料,其乾燥均面層先乾,而後下及;鉛乾料其性均緩;錳乾料均是先期緩乾後轉驟乾作用也。

含高量之金屬根　油中加入乾料愈少者,對於漆膜之情形愈好,故少加乾料而仍有大效者實屬至要之的,卽少加含高量之金屬根乾料,其結果可與多加含少量之金屬根乾料者相同。

此外在賣買方面,設想亦以高量者爲合算今以鈷乾料爲例。

熔性樹脂酸鈷含鈷量約爲百之$2\frac{1}{4}$

沈澱性樹脂酸鈷含鈷量約爲百之6—$6\frac{1}{2}$

沈澱性林諾立酸鈷含鈷量約爲百之$8\frac{1}{2}$

沈澱性哪呋唑酸鈷含鈷量約爲百分之12

設買主購熔性樹脂酸鈷一噸,依其金屬含量計,適等四 cwt. 之哪呋唑酸鈷。貨物之裝置常以 cwt. 小桶爲一單位。火車運費設每 cwt. 爲兩先令六便士。桶費運費自當算入成本之中。依此計之,

則買主所費有不同者如下表矣。

	樹脂酸鈷 磅	先令	便士		哪呋𠯋酸鈷 磅	先令	便士
廿桶價@ 2s 6d	2	10	0	四桶	0	10	0
運費cwt@ 2s 6d	2	10	0	運費	0	10	0
	5	0	0		1	0	0

外加開桶工又爲五與一之比。至於林諾立酸與哪呋𠯋酸金屬間之相差,固屬較小,但亦足以注意也。

乾料除含有高量之金屬外,其金屬全體尤須得能溶解或瀰散在亞麻仁油等之中方爲上乘。茲可舉例以明其重要如下。以市售之林諾立酸鈷溶於亞麻仁油中成爲含 1% 金屬之溶液,但一再加熱後,檢得此皂不甚溶解,濾得清液,用比色器以測定金屬根之含量,僅存0.2%,蓋百之八十之金屬已成棄物。如以哪呋𠯋酸鈷溶於油中者而測定之,則其含量可達 0.98%,幾乎全體溶入油中矣。

林諾立酸乾料或爲劣品,市上所售者亦常有較大之溶度者,惟其品質不一,已可概見其以融合法製成者亦難得全部溶解。

安定度

林諾立酸乾料最易爲氧氣所作用,生成一不溶性的面層膜質,且有時金屬根幷未完全與之化合而成酯類,在分子間之不飽和處,亦有化合之可能,所以須用新製者而不可久藏。

樹脂酸鈷爲氧化所作用,尤爲顯著。在貯藏時,卽能發生高熱,甚而至於自然燃燒。據云樹脂酸鈰不經着火之險,則不能製造。然哪呋𠯋酸乾料爲飽和化合物,性至安定,卽久貯亦不變壞。哪呋𠯋酸鈰之製造時,亦無危險可遇云。

高量溶解度

含什質而言乾料之優良全視其溶解度或瀰散力,使金屬根在油中有極大之催乾能力。

哪呋唑酸可溶於多種有機溶劑,呈清晰透明液體狀,對於亞麻仁油亦然,惟油中含有高量酸價時,時生沈澱。然其沈下者,較林諾立酸與樹脂酸者爲少,苟以適當方法處理之,此種沈澱,仍可免除。

哪呋唑酸乾料之最妙處。爲其有較低之熔點。在 100—130 C 時,卽可熔於亞麻仁油中,毋須過高熱度。故油色淺淡,實因較大之溶解度耳,在有機溶液中,在冷溫時,卽能溶解之。

中和性

樹脂酸乾料中,常含有游離之松香質,然以適合方法所製之哪呋唑酸或林諾立酸乾料中,則無游離酸存在故與鹽基性顏料化合可以不生弊病。

漆膜之影響

製漆和以微量之乾料而得在短時間乾燥,是爲至要。在用融合樹脂酸乾料時,因其金屬根之含量較少,常須多用乾料,有時因多用之故,又能使膜層生脆。苟用哪呋唑酸乾料,則生極强而有彈性之護膜,並無損壞之弊。

分子構造之影響

研究油漆乾料者。常以金屬爲乾燥之主因,但亦未必皆然,例如吾人已知有種物質,竟不含金屬元素,亦可用爲乾料者,是以乾料之非金屬部之關係,亦應計及:

(一)其能瀰散金屬之能力如何

(二)其本身乾燥作用之效力如何

此項研究,所知尙鮮,今日僅知其大意,然仍値得進諸探討焉。

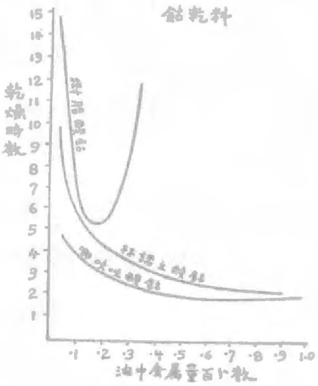
(一) 有機部分之分子構造對於金屬之瀰散力,有極大關係。

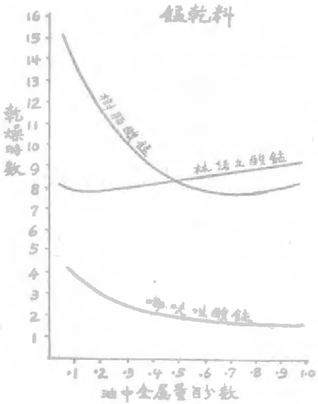
書本中業已述及乾料之應用,其有效分量(金屬根量計)爲

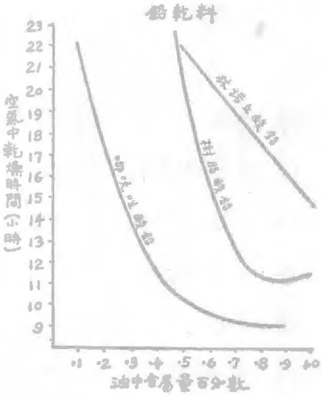
鉛	0.65 %
錳	0.05 %
鈷	0.05 %

如加重分量,其乾燥時間,並不減少,竟或延長之。觀下圖所示各種乾料試驗之結果,可知梗概。

此試驗係以印度亞麻仁油熱至 300° C 並無沈澱析出。酸價 1.45, 碘價 185。在普通空氣中作乾燥試驗,室溫 65°F。亞麻仁油與乾料混合後,經三星期始採用。







攬圖檢視,更得有驚奇之指示,卽在同一之情況之下,得有以下之記錄,如以鈷皂爲例:

0.05 % 之鈷(樹脂酸鈷)與亞麻仁油其乾燥時間爲十五小時半

0.05 % 之鈷(林諾立酸鈷)十一小時可乾

0.05 % 之鈷(哪呋吡酸鈷)五小時可乾

在金屬量過高時,其乾燥時間則相差甚少。

(二)　哪呋吡酸根有無乾燥作用,實無理可信,因其游離酸卽無乾燥作用。但 Bruson 與 Stein 二氏,有提及 Cobalt hydroxy isopropyl benzoate 爲乾料者,能與樹脂酸鈷有一樣催乾效力。然酚(phenolic)類素稱爲極强之退燥劑。何以此時並無作用,殊難索解。

哪呋吡酸乾料之性質

鉛　鉛化合物爲一種黃色性軟之物體,熔點約爲 100° C。不

常單用,在高酸量之油中能結沈澱,但與鈷錳混和時則否。據云其乾燥時間在單用時不能再短於九小時,以之製假漆,用量在 2 % 時須時廿點方燥。但此論以圖所示,則又不然。

錳　爲硬性樹脂質,色褸,熔點在 130—140°C 間。在冷液中沈澱所得者爲淺棕色,但立變深。常用於鉛乾料所不能應用處。及烘漆與硝綿漆(Thining Laquer) 中應用之。

鈷　性硬色紫,樹脂質狀,熔點約爲140°C,在須快乾時應用之。

鋅　輭性灰色狀物質,乾燥力小,在高酸油中能結沈澱。但有特性如下:(一)有劇性殺菌力,可與任何油漆混合無弊;(二)如用黑煤時,有阻止其他乾料不爲顏料吸收之效力。

銅　綠藍色固體,有強性殺菌力。用爲木材或繩索之浸入劑。雖有乾燥性但多量用時,則反阻乾燥也。故普通常與他種金屬混用以改進其品性。如與酐質樹脂 (glyptal resin) 特別組合爲用,可以增進漆膜之堅硬而帶有黏韌性焉。

註:　本篇譯自Paint manufacture Vol. VI No.2 Feb. 1936

M.D. Curwen:—— Naphthenate Driers

一年來英國政府核准之油漆專利案

British Patents, June 1935-July 1936

E.P. 421,420. 假漆　Varnishes, Lacquers. L. P. Kyrides

假漆中之柔韌物以 monosodium ethyl phthalate 與 ethyl chloracetate 凝合而成,或以 monopotassium methyl phthalate 與 ethyl chloracetate 凝合而成,其他類似之 propyl, butyl, benzyl, phenyl sodium phthalate 等都可充作原料。

E.P. 423,876 殺藻船底漆　Antifouling compositions. Smith, Porrit & Dyer, Croydon, Surrey

此漆用氯化橡膠與金屬粉質配合而成,功能殺藻,金屬物之有效者如銅,汞,鋅,砒,及硒和以該屬之氧化物,例如氯化橡膠53份桐油18份,銅粉25.5份,鋁粉3.5份及松節油少許。

E.P. 423,892 有色纖微漆之製造　Lacquers Containing dyestuffs developed in situ. Geigy Akt.-Ges, Switzerland

Triarylmethane 顏料含有一部份能與媒染劑 Mordants 化合,倘與纖微漆和合,並加鉻酸或鉻鹽,稍加熱度,卽能顯現複合而成之色,經久不退。主要之色爲藍,綠,紅三種,例如 Eriochromazurol B, .5g. 在纖微漆 100g. 之中與 .25g. 重鉻化鈉及 .25g. 水楊酸化合加熱後卽現極耐久之藍色。

E.P. 424,597 油漆與水粉漆中之殺菌液　Bactericidal dispersions for oil & water paints. Soc. a Responsibilite Limitée les Bactericides Colloidaux Becco, Paris.

倘以殺菌劑調成乳狀液體加入漆中,功效更大,例如 p-chlor meta-cresol 15份,胡蔴子油100份,水100份油酸鉀40份製成乳液,以20份加入1 Kg之漆,當有極大殺菌效力。

E.P. 424,919 塗料之製造　Coating materials for slate & other building materials. Colloidal Colors, Ltd., Carnarvonshire.

此塗料係一種液體物由氫氧化鐵或鉻或加無電流作用之物質而成。塗刷之膜乾燥後,施以有電流作用之液體物,卽變爲膠體,例如氫氧化鐵和入相當之液質刷於石板上,乾後塗以矽化鈉液,卽成各色之膠膜。

E.P. 425,214 煤膠之應用於油漆　Coal tar pitch in Paints. P. Friedrich, Germany

煤膠漆可由煤膠與綠化脂肪屬烴及芳香屬烴在18－8.0高壓時加熱至130－200°C約$1\frac{1}{2}$小時而成,例如 tar 70, pitch 13, Trichloroethylene 3, benzol 11。

E.P. 425,218 醇化纖微之應用於油墨　Ethyl Cellulose in Printing Inks. I.C.I.

Rotor green Y 四十份, ethyl cellulose 五份,溶於酒精一百五十五份。

E.P. 425,848 鋼鐵建築之油漆施用法　K. E. H. Rodwell, London

鋼鐵物須塗漆三次,以防銹蝕,其程序如下,第一塗油漆須含有水泥若干,第二塗油漆須含煤膠如煤膠(bitumin)爲主要物,在第一塗初乾時卽行塗上,使之黏合,第三塗油漆含有水泥及煤膠二種,此油漆之耐久力全恃第二塗油漆塗刷之適當與否。

E.P. 425.049 牛皮膠在油內之作用　Dewsbury W. G., London

牛皮膠溶於130°C之熱油（動植礦）,能增高潤滑力,5%牛皮膠在植物油,能使油漆中之粉質不致堅結成塊。

E.P. 427,228 塗刷橡皮之漆

橡汁 100，皮膠 1—5，鋇石粉 100，鈦粉 50，松香油 10，乳酪膠 5—20，硫化草蔴油 5.28％，氫 8.35％ 蟻醛 (Fomaldehyde)10，顏料 0—30，水 45—50。

E.P. 427,248 纖微粉爲製漆原料　Du Pont

在碱溶性之綿醲中，以水化法提取纖微，然後加入染料卽成，例如 Ponsol Blue G D 五份溶於水 1000 份，(50°C) 加燒碱六又十分之四份及亞硫酸氫鈉 (sod, hydrosulphite) 五份，在另一器以 sod. cellulosephthalate 廿一份溶於水 1000 份二液混合之後，加熱至 90°C，再加燒碱十份，所得之沉澱乾後磨細成粉。

E.P. 427,438 易溶性之 styrol 人造脂　Standard Oil Development Co. N.J.

Styrene 膠醇化之後，其溶性增加，卽價廉之 Paraffin base 稀薄劑亦可適用，法以氟化硼 (boron fluoride) 複化 styrene 至軟膠程度，再加 amyl Fluoride 醇化之。

E.P. 428,864 人造油　I. C. I.

形似熟油而乾性特快之人造油，可用已將未複化油酸提去之複化油酸與甘油酯化而成，如胡蔴子油酸 1000 份在炭酸氣中加熱至 270°C，經 17～18 小時之後，在 2—3 mm 眞空中蒸溜之 (200°C)，約得未複化之油酸 250 份，以已複化之油酸 158 份與甘油 16 份酯化五六小時(205°C)，再在 245°C 之炭酸氣中熱之，得淡黃之油，其酸價爲 15，乾性特快。

E.P. 428,963 煑油新法　Fritze, Switzerland

煑油之時加四氯化矽或四氯化鈦，能增進複化速率，且乾燥極快，例如胡蔴子油 300 份四氯化矽 10 份，並加礦質松香水 200 份使緩和驟熱作用。

E.P. 429,792 油漆曝露機　Kelvin Ltd. Glasgow, England

試樣受紫外光 12—24 小時後，浸入鹽水中 6～12 小時，如是者約三次計 108 小時，其試驗結果，更甚於單獨浸水 36 小時或

受光 240 小時,試驗器係一小匣,中置鹽水,面有高矽玻璃。

E.P. 430,664 煤膠硝綿混合漆 Deutsche Hydrierwerke A.G. Germany

Esters of cyclohexanol or Ketone 可同作煤膠與硝綿之溶液,溶化後能加大量之稀薄劑不致沉澱,如 benzene 及 benzine, 此漆乾後不回軟,且加塗第二次時亦不溶化,配方(1)Asphalt lacquer 18.5g, nitrocellulose .49g, butyl acetale 1.4g, cyclohaxanolacetate 10g. (2) asphalt lacquer 16, nitrocellulose 2.1, cyclohexanone 11.

E.P. 431,286 瓦皿磁器之塗料 Colloidal Colors Ltd, N. Wales

Hydrated ferric chloride 36 磅溶於清水 8 介倫,再取 5/6 溶於 400 介倫,加燒碱使成沉澱濾乾及洗淨後加入餘剩之 1/6 溶液,調成厚漿.如是者費時約二日,再將此漿加水調至一定鐵質成分,約 20 公分之中含有 .9 公分氧化鐵,然後調入綠色之氧化鉻 21 磅,及黃土 7 磅,施塗後再塗水玻璃液一層,其配法以水玻璃 30 磅冲水 120 磅而成,按以前配方,大約可塗 30,000 方尺。

E.P. 431,951 油溶性人造脂 Saunders, London

Ortho cresol-formaldehyde resin 20 份在 150° C 溶於 glyceryl monolinoleate 40 份,再加 phthalic anhydiede 15 份,在 230° C 加熱一小時,卽成透明之脂。

E.P.432,025 Levulinic acid esters 在纖維漆內之用法 H. A. Auden, Surrey.

15 parts cellulose triacetate, 75 pts. methylene chloride, 15 pts. amyl alcohol, 8 pts. butyl levulinate & .3 pts. resin.

E.P. 432,405 橡膠與油合成之塗料 J.P. Henharen, S. Africa

桐油,胡蔴子油,松香各 25—30 份加熱至 300 F., 加入油酸鈷 .1—3 份,再熱至 540°F..加入橡膠 7—22 份,再熱至 600—650°F.,停火後將橡膠漸漸調溶製成假漆。

E.P. 433,101 鋁矽合成之漆 Metallgesellschaft, A. G. Germany

極細之鋁矽粉，含有5—95%矽，25—70%油料，35%其他粉料，10%稀薄劑合成油漆。此漆有防銹能力，且蓋力極佳。

E.P. 433,333 黑色氧化鐵 Ayers, Penn. U. S. A.

在高壓時氧化鐵質沉澱，可得極細而黑之氧化鐵，製法之主要者爲準確之壓力，熱度，及時間，氧化過度則色棕或紅。

E.P. 433,367 氯化橡膠漆塗於鋁製品之方法 Peintal Soc. Anon, Lausanne

氯化橡膠塗於鋁製品後，因發生氯氣及鹽酸易於脫落，按此法先將鋁之表面氧化後，再塗橡膠，可免此弊，氧化法大致用化學或電化法。

E.P. 434,447 嵌窗之油灰 D. H. B. Cowman, Dorset

（1）石粉（whiting）224磅，清水$1\frac{3}{4}$介倫，胡蔴子油$3\frac{3}{4}$介倫，四氯化炭$\frac{3}{8}$介倫，磨成厚漿，置於不與空氣接觸之罐。

（2）石灰30磅，醋酸鉛22磅，過氧化鉛20磅，磨成細粉，再加過氧化鋇20磅，再磨數分鐘，每成品40磅加凡士林10磅，nitrobenzene $\frac{1}{4}$介倫，另置不與空氣接觸之器，取用之時須在12小時前將（1）15份與（2）1份混合均勻。

E.P. 434,870 氯化橡膠漆 Naamlooze Vennootschap, Zaandam, Holland

（1）1 pt. chlorinated rubber, 3 pts. xylene, 1 pt. oil modified phthalic resin, 1 pt. 厚熱油。

（2）1 pt. chlorinated rubber, 2 pts. xylene, 3 pts. of a solution comprising, 2 pts. oil modified phthalic resin, 1 pt. turpentine。

E.P. 435,003 含有氣體之防銹漆 Fabrik R. Baumheier A. G. Germany

油漆中含有蓄氣之原料如活性炭等，儲藏中和或碱性之氣能漸漸發生，以防銹蝕，碱性者爲ammonia methyl amine, piperidine，中和性者爲ether, propane, organic flourides, lead tetraethyl。例如（1）假漆400份，活性炭135份含6% ammonia 296份，鉛粉115份。（2）船漆：假漆400份，pyridine 180份，鈷皂50份，活性

炭含 2 % nitrobenzene 60 份,銅粉 180 份,松節油 100 份。

E.P. 435,058 纖微漆中之柔韌物質 Dentsche Hydrierwerke A. G. Germany

Dodecyl glycerine ether acetate（硝綿漆用）, Octyl glycerine ether（醋綿漆用）, Cyclohexyl glycerine ether（酒綿用 ether cellulose）。

E.P. 434,350 假漆 (Varnishes) W. K. R. Hartmann, Germany

印刷上所用之罩光假漆,可以乾性油,天然或人造脂,及少數之鎂鋁等皂,催乾劑亦可酌加,並可加各種油溶性顏料配成各色。配方舉例（1）胡蔴子油,硬脂,牛脂酸化鋁及胡蔴油酸化鈷。（2）桐油,硬脂,脂酸化鋁及鉛。

E.P. 437,140 硝綿與橡膠製成之塗料 Cellulosic Rubber Coating Compositions British New-Wrap Co. England

硝綿與橡膠或氯化橡膠溶於 chlorethane 或 aaa-trichlorethane, 用作塗料,可使禦潮,且無透油及臭味之弊,例如硝綿10—20%, 橡膠 2—20 %, diethyl phthalate 0—15%, aaa-trichlorethane 10—30%, acetone 50—70% 乾燥時宜在 70—95°C 之熱氣中。

E.P. 437,302 氯化橡膠製成之塗料 I. G. Farbenindustrie, Germany

混合溶液對於氯化橡膠之溶解性甚大,橡膠之含氯成分須在 54—68% 之間,倘與乾性油混合則至少須 59%,製成之塗料異常清明,遠勝單獨施用一種溶液,硝綿漆之配法—62% 氯化橡膠 21g, 柔韌料 7g, 120°—150°C 𤇆 28g, 酮 12g, butyl acetate 20g, 養化鈦12—15g。油漆之配法——64% 氯化橡膠 20g, 胡蔴子油 15g, 100—190C 𤇆 42g, Amyl acetale 16g, 酮 7g, 及養化鈦粉適度。

I.G.F.P. 7,772,511. 氯化橡膠 Chlorinated Rubber Solution

免除芳香屬溶液之留滯,此案採用酮及酯和脂肪屬及芳香屬之烴,如 acetone, methylethyl ketone, hexanone, alkyl acetates, propionates or formates, white spirit B.P.150—190。

E.P. 436,885 混合纖微酯之製法　Mixed Cellulose Esters, Du Pont de Nemours & Co, U. S. A.

例如 Cellulose acetate-propionate 之製法——取乾燥之白棉 100 份置於 20—25°C 之器皿中,與 propionic acid 600 份混合（含有硫酸三份）,再加 Ketone 80—100 份,此時纖微逐漸溶化,發生之熱在器外冷却之,使不過 40—45°C.,此種混合酯皆可製漆且與多元醇化合者又可製成黏料及靭料。

E.P. 438,887 尿素與蟻醛製成之黏料　W. Kraus, Germany

水溶性之黏脂可由尿素與蟻醛製成,充作黏料,製法之成分必須適量,如尿素與 hexamethylene tetramine 爲 1—10:1 之比,formaldehyde 與 urea 爲 1—2:1 之比,如有過量則成不溶性之脂,再混液中須有酸價（pH）3, 使成水溶性之脂, 例如（22.7%）氨 250 份（以容量計）與蟻醛 375 份化合後,加 hexamethylene tetramine 與尿素 150 份 (重), 蟻醛 244 份 (容), 草酸 2.5 份（重）（溶於蟻醛）之混合液而煑之,並時時調動,待水份蒸發至 465 重量,斯時白色之漿,易溶於水,可以用作黏料, hexamethylene tetramine 與尿素之比爲 1:3, 尿素與蟻醛之比爲 1:1.3。

E.P. 439,312 氧化鈦與硫酸化鈣之混合　Titan Co. U. S. A.

氧化鈦 40—60% 與硫酸鈣 60—40% 經精密混合之後,其加色度勝過淨氧化鈦,尤勝於機械混合,其法以硫酸鈣漿加入硫酸鈦及鐵（密度 1.4）約含 6—12% 氧化鈦及極少之硫酸,加入之量約成乾粉含有氧化鈦 50% 與硫酸鈣 50%,其間須經加熱,過濾,洗漂,烘灼等手續。

E.P. 439,835 蟲膠之代替品　E. E. Dutt., London

含油果實之外果皮與有機鹽基加水分解,即成一種類似蟲膠之品,例如橄欖之外皮經過四十眼篩布後,在 105° C 調入萮胺,使膠狀物水分解成液體,過濾以去過量之萮胺,另取萮

胺一份洗之,嗣後仍可以此爲水分解之用,初次濾得之萘胺以水洗去什質用眞空法蒸餾之,所得膠質物經熱榨機除去餘剩之萘胺,此膠之性質極似蟲膠,碘價爲8—10。

E.P. 439,946 不銹鐵用爲製造油漆之粉料　C.D. Ryder, Australia

不銹鐵屑加入油漆,能使漆膜堅牢耐久,因其形狀不一,在漆膜內之組織甚爲密切,與普通粉料迥然不同,船漆以人造膠2.76%,鉛皂5.6%,桐油8.8%,熟蘇子油4.4%,松節油14.4%,松香水9.1,鈷皂.012%,鐵屑60%配成;磁漆以人造膠2.5,硬松香.175,鉛皂.05,鈷液(2%鈷).06,胡麻子油2.625,桐油5.34,松節油14.25,鐵屑75配成。

E.P. 440,371 氯化橡膠之用爲防銹塗料　I.G. Farbenindustrie

此項塗料係用氯化橡膠不能皂化之韌料,及比重在5以上之粉料配合而成,性能防銹禦水,且富有粘性,遠勝以油料配成者,其不能皂化之韌料乃指 Chlorinated diphenyl, Coumarone resins 及硫與萘類之化合物而言,粉料之適用者爲硫化鉛,鉻酸化鉛,紅丹,鋅粉及鐵丹等,茲舉一例:

氯橡膠(65%氯)20, Benzyl naphthalene 2, Chlordiphenyl (57%氯)3, white lead 12, 鐵丹 10, solvent 52, chlorinated naphthalene (50%氯)1, 以此爲底層,然後再塗任何油漆,均能得美滿結果。

E.P. 440,575 乳化液之配合　E.I. du Pont de Nemours & Co. U. S. A.

重金屬鹽之製自多元醇(8)與硫酸者,爲最有效之乳化劑,以 n-lauryl sulphuric acid salt 一份溶於石油五十份,再以另一液有醋酸鉛.25份水48.25份和入即成乳液,若再加多量之石油,亦無變化,此法亦可應用於水與胡蔴油之乳化以製油漆。

E.P. 440,889 塗料　Groves, W.W. London

粉料如紅丹,氧化鎘,或二者合用與酒溶性之酚質樹脂混合,

可不加熱度而使堅硬。

E.P. 442,603 尿素蟻醛配成之漆 Nowack, A. G. Germany

此漆製法係用水與水溶性之有機溶液及尿素等化合,然後將水蒸去,例如 200 urea, 50 thiourea, 565 formaldehyde (35%), 50 glycol monoacetate, 48 soda lye (20%), 3 sod. carbonate 蒸溜二小時,然後去水 200 公分,再加適量之 glycol 及glycol monoethyl ether, 再去水 120 公分,再加 70 glycol monomethyl ether 及 50 monoethyl ether. 卽成。

E.P. 427,228 適用於橡皮物件之塗料

此漆之主要品爲橡膠,蛋白質黏性物及使其不溶解之藥劑,例如橡膠 100, 皮膠 1—5, 硫酸化鋇 100, 氧化鈦 50,松香油 10, 乳膠 5—20. 硫酸化草蔴油 5, 氨（28%）8, 蟻醛（35%）10, 顏料 0—30, 水 700—800。

E.P. 427,248 纖微料之爲製漆粉料 E.I. du Pont de Nemours Co. U. S.A. 5 Ponsol blue G D(anthraquinone dye)溶於水 1000,在 50°C 加 6.4苛性鈉及 5 亞硫酸鈉,另一器具盛 21 sod. cellulose phthalate 及水 1000, 溶解後加入第一液,加溫至 90°C.,再加 10 苛性鈉,使完全水化,所得沉澱冷後過濾沉清,烘乾磨細卽成。

油漆工業雜誌錄要

Paint and Varnish Production Manager.

June, 1935,—May, 1936.

1. 臨界需油量之簡易檢定法(*Rapid method for the determination of the critical oil requirement; H. Wolff, G. Zeidler; Vol. XII, No. 6, P. 7*)

本篇首述『臨界需油量』之定義,及其與『最適需油量』(*Optimum oil requirement*)之異同;其檢定在油漆工業上,對於用油之經濟及煮油法之改良,有莫大裨益。

此法之特點,在能避去冗長算式,而代以簡易之圖解法。所需儀器,主要者爲小漆磨及『透平』式粘度計 (*Turboviscometer*) 各一具,每次檢定,約需二小時半。

2. 新式防銹塗料 (*New protective coatings for the protection of structural steel; B. Scheifele; XII, 6,14; XIII, 1,32*)

新式防銹塗料,概括防銹油漆,硝棉漆,瀝青漆及其他防銹混合劑如氯化橡膠製劑等四大類。防銹油漆價較廉,效用亦著,故最爲普及;硝棉漆極易乾燥,防水性强,亦不易受化學藥品之侵襲,惟應用時,諸多不便,又不能耐久故除特殊需要外甚少用者;瀝青漆及橡膠製劑等,則只用於多水及時遇酸礆之處,因其對於此三者,具有絕大之防禦性也。新興材料如人造桐油,人造樹脂,氯化橡膠及苄化纖維(*Benzyl cellulose*)等,均各有其獨到之功能。數種混合使用,尤能互補短長而收絕好效果。

本篇對於上列各點,均有確切討論,他如關於底漆及面漆之新理論,紅丹及鋁粉之防銹原理,以及鋼鐵防銹方法與施用塗料之正確手續等,亦指述甚詳。

3. 新式油溶性酚質樹脂(*Newer types of phenolic resins in oil varnishes; G. Dring; XII, 6,24.*)

油溶性酚質樹脂具有空前之强大抗蝕性,故其應用於油漆製造工業,已早著成效,幾成不可或少之原料。其最大缺點爲於日光中曝露稍久,則變深黑色,故用於注重彩色之美術漆中,不甚合宜。

酚質樹脂之改良,日新月異,前此已有不變色之產品出售,最近數種出品,雖因試驗不週,尙未普遍採用,其曾經檢定之優點則已有下列數端:——

1. 曝於日光不易變色。
2. 在油中,不必加熱亦能溶解。
3. 有數種當與油同煑時,且能起連續複化作用,最後成爲高熔點之硬質樹脂,用製油漆,光彩特强。
4. 油漆中含有少量之樹脂,卽能乾燥甚速。
5. 能增加漆膜之硬度,彈性,耐久性及抗礆能力。

用此種樹脂造漆,其熬煑手續與常法略有不同,本篇載有多次試製之經過情形及其結果,對於分量,熱度及時間三者有精密之商榷。

4. 鉻酸鋅 (*Zinc chromate; Staff of Journal; XIII, 1 ,12*)

鉻酸鋅爲黃色粉末,俗號鋅黃粉 (*Zinc yellow*);與普魯士藍混合,卽成鋅綠。此二者用於造漆已有時日。近來因發現其有防銹特性,最適宜用於鋁合金之底層漆,故更受重視。

本篇敍述鉻酸鋅,及其複鹽與鹽基式鹽之各種製法,甚爲詳盡,並介紹該項商品之檢驗標準 (*Specification*)。

5. ⿰火侖化纖維漆 (*Benzyl cellulosc lacquers; Louis Light; XIII, 1, 18.*)

自硝棉漆盛行後,熗化纖維及其他各種纖維衍化物復相繼而起;其効用,較諸硝化纖維多有過之者。市上所售之熗化纖維,實爲 *Dibenzyl cellulose ether.* 具有下列諸特點:——

1. 不能燃燒,
2. 不畏淡性酸礆,
3. 不畏日光,
4. 能禦水,
5. 放於沸水中不變軟,加熱至 170°C 則熔解,惟不生化學變化。

以與硝化纖維及醋化纖維相比,則熗化纖維有最强之抗禦光,水及其他化學藥品之能力,故所製塗料,應用於海船,冷藏庫及花房等處,無不相宜。

熗化纖維漆之製法,略如硝棉漆,用法亦同。溶劑以八份 *Benzol* 與二份乙醇之混合液爲最佳,若用 *Xylol* 與少許高沸點之溶劑如 *Butyl alcohol, ethyl lactate, butoxyl* 等之混合液爲溶劑,則所成之漆質,性黏,可用刷塗之;柔韌劑如 *diethylphthalate, dibutylphthalate, triphenyl phosphate, triisobutyl phosphate, glycol ditolyl ether* 及 *Aroclar 1254,* 人造樹脂如 *glyceryl ester of rosin, glycerol-phthalic anhydride resin* 及 *chlorinated diphenyl resin* 等,均可應用。

6. 漆膜之結成,及其對於金屬面之保護能力 (*The formation of paint films and their protection of metal; Hans Wolff; XIII, 2,7*)

油漆膜因由複雜之物理及化學變化而結成。其變化內容,雖經多數學者之研究,尚屬渺茫,惟此膜爲一膠狀體,則已無疑。其結構與組織,除油漆自身之因素外,在乾燥時直接受外界情狀變化之影響;故每種油漆之防銹能力,亦隨用漆時之氣候,所在地及其所保護金屬面之狀况,而有不同。作者在數年前已創此說,近據試驗結果復發現:——

1. 同一油漆,在高溫（30°C）乾結者,漆膜中游離酸含量較在底溫度（15°C)乾結者爲少。

2. 在同溫度乾結,經强光（如水銀弧光）照射者,游離酸含量更少。

漆膜之游離酸含量,與其防銹效果有絕大關係,蓋當漆膜潮濕時,此酸能溶解而侵及所接觸之金屬面也。

7. 抗霉油漆之改良(*Development of mildew-resisting paints; L. P. Hart; XII, 2, 12*)

本篇爲一簡略之研究報告,以不同份量之多種殺霉劑,加入於三種特製油漆中,製成二百餘種漆樣。在美國 *Florida* 曝露後,驗無霉點而漆面完好者有十餘種。據作者觀察所得,下列數點頗值注意:——

1. 在塗抗霉漆於一物面之前,需用放大鏡檢視此面是否已有霉點。

2. 如發現已有霉點,須先用皂水或硷水洗淨之。

3. 在普通油漆中,加入適量之硬性假漆,使其漆膜加硬,亦能防霉。

4. 若用二氯化汞, *phenyl mercury acetate*, 或 *ammoniated mercury*, 則可臨時加於面層用漆中。份量約爲每500至900份漆中,加入一份。

5. 深色漆,可用紅色*Cuprous oxide*,綠色漆,可用*Paris green*（約10%）。

6. 廚房,烟廠及紗廠等悶熱潮濕之處,不宜用銅,汞等劇毒製劑,但可用 *thymol* 代之。

8. 製造硝棉漆用之柔韌劑（*Plasticizers in nitrocellulose lacquers, Alfred Kraus; XIII, 2, 16*）

收集四十一種市上所售新舊柔韌劑(包括最新出品如 *glyacol, cetyl acetate, olein alcohol acetate & plasticizer REA* 等),

而研究其對於硝棉漆之膠化(*gelatinization*)能力,粘度之改變及漆膜性能,如拉力,伸長量及耐光性等之影響。所作試驗,甚饒興趣,惜限於篇幅,只略述概要,對於柔韌劑之選擇可作有力參考。

9. 纖維漆之試驗法(*Lacquer testing; H.E. Eastlack; XIII, 2, 20*)

本篇討論作者對於色彩及光澤(*gloss*)測定法之研究經過,並介紹人工曝露及數種簡易之性能試驗法。

10. 用統計法研究戶外用油漆液料之耐久性(*Statistical study of the durability of vehicles in exterior paints; Hans Wagner; XIII, 3, 7*)

本篇之目的,在於試驗顏料在漆膜中對於液料原有耐久性之影響,以研究其是否能補救劣等液料之缺點。法用十餘種液料,及五十餘種顏料製成各種漆樣,塗於不同材料所製之試板上,經三年之懸空及水底曝露試驗後,統計所得結果約爲:——

1. 在水中曝露結果不良者,所用液料計有

(*a*)亞麻仁油,及亞麻仁油假漆,大半因吸水澎漲,終至破壞漆膜。

(*b*)厚熟油(*stand oil*),假漆(*patent varnish*),及混合硝棉漆(*blended nitiocellulose lacquer*)塗於平滑物面者,大都全部剝落(*Peeling*)。

(*c*)硝棉漆大都易於鱗落(*scaling*)。

(*d*)上等人造樹脂假漆,及無光漆,大都易於(*blistering*)生疱。

2. 色料依曝露結果,可分爲三類:

(*a*)結晶性不透光者—如 *iron oxide, chrome oxide green, naples yellow* 等。

(*b*)易起化學分解者—如 *Chromates, chrome green, zinc green,* 及 *cadmium sulfides* 等。

(c)半結晶性,或非結晶性顏料——如 *milori blue, ultramarine-blue, victoria green, hydrated chrome oxide green* 等。

平均耐久性,以 *a* 類爲最大, *c* 類爲最小。每一類中,亦有能與某種液料合用,而得絕佳效果者,本篇有表詳列之。

3. 同一漆樣,塗於金屬面者,其耐久性,較諸塗於木面者爲小。

4. 厚熟油摻用於各種油漆中,能絕對增大其耐久性,故對於厚熟油製煉法之改良亦曾提及。

11. 化學顏料(*Chemical colors; A.F. Brown; XIII, 3, 14*)

本篇敍述多種化學顏料之來源,性質及用途。

12. 蟲膠之代用品(*Shellac substitute; C.F. Mason; XIII, 4, 18*)

合成蟲膠之製造,雖已有數法,惟均因成本過巨,未經採用。目下蟲膠漆之代用物,多以醇溶性天然樹脂(*spirit soluble manila copal*)加蠟製之。本篇略述其製法。

13. 油漆之褪色(*Investigation of color permanency; a progress report; XIII, 5, 22.*)

本篇搜集關於油漆褪色問題之文獻,而總述其概要。

14. 油漆之殺菌力及新殺菌漆(*Paints–their disinfectant properties-steps in the production of a germ proof film; S. Wetchler, A. Lewis, and F. Battline; XIV, 1, 12*)

用標準手續,繁植 *typhoid bacillus* 及 *staphylococcus aureus* 微生物於漆膜上,以檢定其殺菌能力。所得結果約爲:——

(1)市售及按照普通方式所特配之油漆,最初均能殺菌,惟塗下一至三星期後,殺菌力卽已完全消失。

(2)任何顏料,油類,天然及人造樹脂,不能改變漆膜之殺菌力。

(3)加消毒藥劑如 *phenol, cresol* 及 *iodoform* 等於油漆中,塗上十五日後,殺菌力亦全部消失。

(4)若用氯化油製漆(有效含氯量爲油之百分四),則其殺菌力能維持至 3—4 年之久,且此種油漆無礙衞生,亦無特殊臭味;製造氯化油祇須通氯於油中卽得。

(5)此漆乾後,用皂水洗之數次,亦不減少其殺菌力。

15. *Para coumarone-indene* 人造樹脂 (*Paracoumarone-indene resins; XIV, 1, 26*)

從煤乾溜產物中,提出 *coumarone* 及 *indene* 後,經特殊複化手續,卽成此種樹脂。具有不畏光,熱,酸,礆,水,鹽,無毒,無臭,無味,不能傳電,氧化,礆化,及爲中和性諸特點;已爲油漆及其他工業所採用。市售者,自粘液至高熔點固體,共有數十種之多。本篇只詳其特性及對於油漆製造之用法。

16. 橡膠之用於油漆製造(*Rubber in Paints and Varnishes; XIV, 2, 12*)

於油漆中,加入少量橡膠,可以增加其流動性,同時顏料亦不易沉澱。此種含橡膠油漆,乾燥甚速,以製無光漆,底層漆,及調合漆等均甚合宜。本篇係述橡膠之各種用法。

17. 油漆工業之小進展(*Some recent developments in the paint industry; part 1 J.R. Stewars; XIV, 3, 28.*)

本篇略述下列數種新事物:

1. 防止人造樹脂磁漆發生橘皮形(*Crange-peel effect*)之研究方針。

2. 混濁度標本

醫藥業用克拉克氏混濁度計(*Clark Turbidimeter*),似可用以量假漆,樹脂及溶劑之混濁度(*turbidity*); 此計係加浮懸物於動物膠(*gelative*),以製成已知其混濁度之標本一套,分裝於玻管中,裝漆樣於另一玻管與此計相較,卽能比定其混濁度。

3. 新發現之 *Po-Yok* 油

Po-Yok 樹果中含油量及60%, 此油榨出後,質厚,色草黃,

有數種特性與桐油相似,用途尚在研究中。

4.石油質溶劑之新分類法：——

此法爲*Toby*氏所創議,係根據其與*Kauri-Butanol*溶液之最高混合量,詳細標準仍在研究中。

18. 通俗顏色學(*The Colorists Educational Program; A.C. Watson; XIV, 1, 7; XIV, 3, 7; The Psycho-physics of color; same author; XIV, 4, 7; XIV, 5, 7*)

此係一長篇著述,用最通俗之語調,介紹最新顏色學之理論及方法。

19. 油膜之變黃及其防禦法 (*The yellowing of oil films & its prevention; A. Eibner; Part I, XIII, 4, 13; XIV, 4, 103; part II, XIII, 6, 10; Part III, XIV, 2, 7; Part IV, XIV, 3, 12.*)

油膜變黃之正確現象,統觀歷史上之記載及最近試驗所得,約有下列數端:——

1.油膜乾後,置於黑暗中或有陰影處,經數星期卽變黃色若再曝之陽光中七八日後,卽又轉白。

2.數種色料及催乾劑,對於油膜能起一種媒介作用,促其變黃。

3.厚熱油(*Bodied oil*)之乾膜,在黑暗中絕不變黃。

4.新油膜在黑暗中加熱至110°*C*,經數小時卽變棕色。

5.油膜置乾空氣中,雖不與日光接觸,亦不變黃。

據作者意見,歸納以上現像,可得下列之解釋:——

油膜自身吸水澎漲之作用,實爲主因,間接受外邊空氣濕度之影響,照射光線之强弱則間接之又間接者也;蓋陰暗處,空氣多潮濕,油膜之吸水量因而增加,故易於變黃;厚熱油不變黃色亦係此理,蓋複化油不易吸水也。

油膜吸水後所以變黃者,據多數作家之意見,爲一種化學變化;初步理論,本篇末後兩章有詳細討論。

20. 用比較法試驗防銹膜性能之新工具 (*A new method of comparative testing of Protective Coatings, A. Kufferath, XIV, 4, 20*)

新近設計一種顯微鏡,用以觀察防銹膜面經曝露後所起變化之情狀,加以比較,卽可推測其防銹性能及膜層破壞之原因,手續簡單,結果精確。

21. 漆色與散熱效率之關係 (*Paint & its relationship to heating efficieny; J.R. Stewart; XIV, 4, 26*)

水汀散熱器,習慣上均塗以銀色或金色之金屬漆;據多數研究結果,均認爲塗金屬漆者,所散熱量反不如塗白色或淡色漆者之多,所差約有10%。

22. 美國 *California* 產沙汀魚油 (*California Sardine & other oil; R. C. Rollins, XIV, 5, 12*)

此篇爲通訊稿,略述該處沙汀魚油之產銷狀况,及其性質與用法等。

23. 油漆黏度與其他物理特性之關係 (*Viscosity and its relationship to other physical properties; J.R. Stewart; XIV, 5, 16*)

此篇係研究黏度與乾燥速度,膜層厚度,塗蓋量 (*Spreading rate*), 塗刷性 (*Brush ability*) 及乾膜硬度等之關係,惟試驗範圍,只限於特製之酚質樹脂與桐油所製之漆。

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化學系畢業論文概要

本年度化學系,共有四年級生十六人。其中黃允中一人,已在上年度呈繳論文,列入上期報告;此外十五人共呈論文十六篇。茲撮述每篇內容以見梗概。

1. 酒精製造醋酸之研究（范　棠）

酒精在氣體狀況之下,用接觸劑氧化,可得乙醛;復用相當接觸劑可使在液體狀態之乙醛變成醋酸。本題曾用銅,鎳,氧化銅及氧化銅與氧化錳氧化鈷氧化鉻等之混合物爲接觸劑,檢定(1)空氣與酒精之比例,(2)混合氣體之流速,(3)接觸劑之溫度等,對於酒精氧化之影響。復用鉻錳銅等醋酸鹽,試驗乙醛氧化成醋酸之最適宜狀況。

2. 低質澱粉之精製（萬葆德）

低質澱粉含有雜質甚多,色帶褐黃。曾用各種機械分離及化學處理方法,加以精製,結果以漂白粉爲最佳。加入醋酸,收效尤速。成品經分析與檢驗,證明其品質與市上上等澱粉相等。

3. 結晶穀酸鈉 (Monosodium-d-glutamate) 之試製（萬葆德）

市售調味品均係粉狀,遇潮易硬結,且含有雜質甚多。本題試製晶體穀酸鈉,從提淨穀酸入手,中和時用精密物理方法節制,可得白色結晶。

4. 桐油酸與多元醇製造合成油之研究（郭鍾福）

（見研究報告中）

5. 鋁矽酸鈉淨水劑之研究（林仁穆）

本題目的在研究增進鋁矽酸鈉之堅度,以免久用裂碎之弊。經用水泥,硅藻土,澱粉等物爲粘合劑一一試驗,發見加入適量之某物質,其淨水能力,可增加數倍。此外并探知製造時烘乾得法,並無用粘合劑之必要。

6. 皂莢精之提取（馮　盈）

提取方法經比較結果,以熱水浸提後,再以稀酒精沉澱最爲適宜。其產品礆化價爲200,起沫價爲10000。其祛汙能力,以實驗洗濯方法檢定,較皂爲遜,以石墨懸浮方法檢定,則甚佳。用以爲泡沫滅火機之固定劑,其發生之泡沫,匀細而能持久,較平常所用物質爲佳。

7. 豆酪素製膠合劑之研究（張丙官）

（見研究報告中）

8. 低黏度硝棉之試製（林厥達）

（見研究報告中）

9. 鎢之提取（陸家振）

鎢礦提取方法,通常成氧化鎢後,在高溫度加氫還原,方得鎢粉。今擬利用重鎢酸錏及氨之加熱分解性,可得新生狀態之氫及氧化鎢,還原作用,較氫爲速經試驗結果,已得相當之證明。

10. 甲笨氧化之研究（張西緣）

以甲笨氧化,可成香料業所需要之不含氯質之笨甲醛。所用氧化劑爲各種氧化錳,可用不同之方法製取。試驗結果,以自硫酸錳及過錳酸鉀製成之三氧化二錳爲最佳。

11. 豆酪素製水粉漆之試驗（孫　衛）

（見研究報告中）

12. 海州磷礦製肥料之試驗（甘懷新）

礦石分析結果得氧化磷百分之二三,經硫酸處理之試驗,探

知以用酸占礦石重量百分之六七至七四爲較宜。

13. 耐酸琺瑯質之試製(錢樹聲)

就各方式配合之耐酸琺瑯製成後,取小塊浸入濃鹽酸三小時,檢驗其損失之重量,最佳樣品,每平方公分只損百分之七厘。

14. 標準砂之研究(童登琮)

標準砂爲水泥檢驗所必需。吾國尚習用外國標準,急應就國產細砂,比較試驗。以期尋得一適合代用之細砂。經試驗結果,發見英美德各國標準砂,含氧化矽在百分之九八以上;而國產甯波砂只百分之七六零,殊不合用。

15. 生漆之研究(周恕安)

(見研究報告中)

16. 雜醇油提製硝棉漆溶劑之研究(丁憲祜)

(見研究報告中)

新書介紹

I. 書　名　The Paint Laboratory Note-book.

著　者　John Stewart Remington.

出版者　Leonard Hill, Ltd. (December, 1935).

內　容　Tests for white and colored pigments, oils and turpentine including a list of standard solutions and their constituency and a brief account of the flame test, and important physical properties. In the last chapter, useful data for works chemist and the works manager are compiled.

附　註　本書共68頁;所述試驗方法,均屬簡便易行,儀器之選擇亦以簡單爲主。

II. 書　名　Physical and Chemical Examination of Paints, Varnishes, Lacquers, Colors. (Seventh Edition).

著　者　Henry A. Gardner, D. Sc.

發行者　Institute of paint and Varnish Research, Washington, U.S.A., (October, 1935).

III. 書　名　Aluminium in the Chemical and Food Industries.

發行者　British Aluminium Co., Ltd.

內　容　General properties and uses of aluminium and its alloys, and the methods of testing the corrosion resistance of the bodies; protective coatings for aluminium surfaces; the principal methods of jointing light metals; the erection and maintenance of aluminium equipment; action of organic and inorganic substances on aluminium, such as the action of linseed oil, madder lacquer, etc.; and aluminium plant designed to meet the requirements of illustrations.

附　註　本書爲小册式,共121頁、

IV.	書名	A Shellac Patent Index.
	著者	R. W. Aldis, Ph.D.,
	發行者	Indian Lac Research Institute, Namkum, Ranchi, Bihar and Orissa, India.
	內容	Short general description of the use of shellac in industries, and classified abstracts of patents on shellac taken out during the last half century.
	附註	本書共115頁,售價Rs. 2/8.
V.	書名	油漆製造程序圖解
	著者	上海永固造漆公司
	內容	此圖係五彩石印掛圖格式內列應用各種原料機器及配製方法極合職業學校授課時解說之用如有需要可以函索

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