Improvement of Drying Properties of Tobacco Seed Oil

by

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Summary : This research, after summarizing the views of different investigators regarding the drying properties of tobacco seed oil, points to the important place tobaccoseed oil could occupy in the Turkish drying oil industry.

In the courses of the experiments, four oil-modification methods commonly used for other semi-drying and drying oils were applied to tobacco seed oil and the results obtained are summarized below :

1. Tobacco seed oil was oxidatively polymerized by blowing with pure oxygen at 105, 150 and 195 C° and the changes of the chemical and physical properties of the oil were investigated. The drying properties of the polymers to which Pb, Mn and Co driers had been added, and the water resistance of the films formed were also investigated. The investigations have shown that, for all drier combinations, the best films were formed by tobacco seed oil blown at 195 C°.

2. Tobacco seed oil was thermally polymerized at 260, 300 and 320 C° under CO_2 atmosphere and the changes during heat polymerization in the chemical and physical properties of the oil were investigated. The drying properties of the resulting polymers and the water resistance of the metal catalyzed films were also investigated.

The polymerization rate constants for each temperature were calculated and compared to those calculated from data found in literature. It was found that the polymerization rate constant (K) for polymerization at 300 C°, was within the limits of the K values given in the literature for linseed oil processed at the same temperature. It was also found that there is no difference between the properties of paint films prepared from tobacco seed oil polymerized at 300 C° and polymerized linseed oil at the same temperature.

Furthermore, exposure of 2 years to atmospheric conditions showed that polymerized tobacco seed oil paint film underwent less yellowing than the film from linseed oil.

3. Vacuum distilled tobacco seed oil fatty acids were esterified with polyalcohols like pentaerythritol, sorbitol and tetramethylolcyclohexanol and the characteristics of the resulting esters were investigated. Polymerized forms of these esters were also prepared. The drying properties of the metal catalyzed normal and polymer esters and the characteristics of the films obtained from these esters were investigated.

It could be proved that these polyalcohol esters have better film forming characteristics than unmodified tobacco seed oil The best results obtained from the pentaerythritol ester.

Varnishes were also prepared from the polymerized polyalcohol ester of the tobacco seed oil fatty acids and the characteristics of these varnishes were investigated. Resistance of the above varnish films to water and to the aqueous alkaline and acid solutions were determined and the results compared to those obtained from varnishes made from polymerized tobacco and linseed oils prepared with the same manner.

As a result of the above findings, it was seen that the pentaerythritol tobacco seed oil fatty acid ester varnish is superior to the linseed oil varnish containing the same synthetic resins.

4. The addition reaction of tobacco seed oil with 10 % maleic anhydride and 10 % fumaric acid were investigated, and it was found that the reaction with maleic anhydride was completed in less than one hour, whereas, the reaction with fumaric acid took in 1.5 hours for completion.

Tobacco seed oil alcoholyzed with different polyalcohols, reacted with 5 % maleic anhydride and fumaric acid and the resulting adducts were investigated.

It could be concluded from the above that this modification with dibasic acids was a suitable method for producing satisfactory film forming adducts from tobacco seed oil.

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Özet : Bu çalışma Kuruyan yağ endüstrisinin kullandığı yağlara kısa bir göz attıktan sonra, tütün tohumu yağının Türkiye Kuruyan yağ ekonomisinde oynayacağı büyük rolü belirtmekte ve şimdiye kadar birçok araştırıcılar tarafından tütün tohumu yağının kuruma özellikleri hakkında zikredilen muhtelif mütalâaları incelendikten sonra, tütün tohumu yağının kuruma özelliklerinin geliştirilmesi için muhtelif tâdil metodlarının tatbikinden elde edilen neticeleri vermektedir.

1. Tütün tohumu yağının saf oksijen ile 105, 150 ve 195 C° lerde oksidasyon polimerizasyonu neticesi, tütün tohumu yağında meydana gelen kimyasal ve fiziksel değişimler incelenmiş ve meydana gelen polimerlerin Pb, Mn ve Co sikkatif metaller muvacehesinde kuruma özellikleri ve meydana gelen filimlerin suya karşı mukavemetleri araştırılmıştır. Filim verme özellikleri bakımından en uygun okside tütün tohumu yağının 195 C° de okside edilen yağ olduğu neticesine varılmıştır.

2. Tütün tohumu yağı 260, 300 ve 320 C° lerde CO_2 atmosferi altında ısı polimerizasyonuna tâbi tutularak tütün tohumu yağında meydana

gelen kimyasal ve fiziksel değişimler ve elde edilen polimer yağların Pb, Mn ve Co sikkatif metaller muvacehesinde kuruma zamanları meydana gelen filimlerin suya karşı mukavemetleri incelenmiştir. Polimerizasyon sürat konstantları her temperatür için hesaplanarak, literatürde verilen değerlerden hesaplanan sürat konstantları ile mukayese edilmiş ve neticede, 300 C° de tütün tohumu yağı polimerizasyon süratinin literatürde keten tohumu yağı için ayni temperatürde verilen sürat konstantları sınırları içinde olduğu görülmüştür. 300 C° de polimerize edilen tütün tohumu yağı ve polimerize keten tohumu yağı ile hazırlanan boyalar arasında hiçbir fark olmadığı, bilâkis 1 sene harici şartlarda muhafaza edilen boyalarda tütün tohumu yağı ile imal edilende daha az sararma meydana geldiği görülmüştür.

3. Vakumda distile edilmiş tütün tohumu yağ asitleri pentaeritritol, sorbitol ve tetrametilolsikloheksanol gibi poli alkoller ile esterleştirilerek meydana gelen esterlerin kimyasal ve fiziksel özellikleri tâyin edilmiş ve bu esterler polimerize edilerek polimer esterler hazırlanmıştır. Elde edilen normal ve polimer esterlerin Pb, Mn ve Co gibi sikkatif metaller muvacehesinde kuruma özellikleri ve meydana gelen filimlerin özellikleri tayin edilmiş, neticede bu esterlerin tütün tohumu yağından daha üstün vasıflara sahib oldukları görülmüştür. En uygun neticeler pentaeritritol ve tetrametilolsikloheksanol ile elde edilmiştir.

Poli alkol esterlerinden sentetik reçinelerle vernikler hazırlanmış ve bu verniklerin özellikleri tayin edilerek, elde edilen filimlerin suya, alkali ve asit çözeltilere karşı mukavemetleri incelenerek, ayni reçinelerle ayni şekilde polimerize tütün ve keten tohumu yağlarından yapılan verniklerle mukayeseleri yapılmıştır. Neticede, pentaeritritol tütün yağ asidi fenolik reçinesi verniği birçok bakımlardan keten tohumu yağı verniğinden üstün olduğu sonucuna varılmıştır.

4 — Tütün tohumu yağı % 10 maleik anhidrit ve fumarik asit ile katılma reaksiyonuna sokularak, reaksiyonun gidişi incelenmiştir. Maleik anhidrit ile reaksiyonun 1 saatde, fumarik asitle olan reaksiyonun ise 1,5 saatde neticelendiği görülmüştür. Muhtelif poli alkoller ile ester değişimi yapılmış tütün tohumu yağları % 5 maleik ve fumarik asit ile reaksiyona sokularak muhtelif polimer yağlar elde edilmiş ve bu yağların kuruma özellikleri, jelasyon müddetleri ve filimlerin özellikleri incelenerek, bu tadil metodunun tütün tohumu yağı için uygun bir metod olduğu neticesine varılmıştır.

Zusammenfassung

Nach einem kurzen Überblick über die Pflanzenfette, die man gewöhnlich bei der Herstellung organischer Anstrichmittel verwendet, werden die Meinungen einer Reihe von Forschern über die Trocknungseigenschaften des Tabaksamenöls zusammenfassend zitiert. Es wird auch auf die wichtige Rolle hingewiesen, die das Tabaksamenöl in der Türkischen Anstrichmittel-Industrie einnehmen sollte.

Im Laufe der folgenden Forschungsarbeit wurden vier der häufig bei halb-trocknenden und trocknenden Ölen angewandten Öl-Modifikations-Methoden auch für die Modifikation des Tabaksemenöles angewandt und folgende Resultate erzielt.

1. Tabaksamenöl wurde oxidativ polymerisiert, indem reiner Sauerstoff bei Temperaturen von 105°, 150° und 195° C. durchgeblasen wurde; die chemischen und physikalischen Veränderungen, die diese Behandlung hervorriefen, wurden studiert. Die Trocknungseigenschaften der so entstandenen Polymeren, denen Katalysatoren wie Co, Mn und Pb. hinzugefügt worden waren sowie die Wasser-Widerständsfahigkeit der metall-katalysierten Filme wurden geprüft. Diese Versuche zeigten, dass mit allen Sikatif-Kombinationen die besten Filme mit Tabaksamenöl erhalten wurden, das bei 195°C geblasen worden war.

2. Tabaksamenöl wurde in einer CO_2 Atmosphere bei 260°, 300° und 320°C polymerisiert, und die Änderungen der chemischen und physikalischen Eigenschaften des Öles, die während dieser Behandlung auftraten, beobachtet. Auch wurden die Trocknungseigenschaften der so erzeugten Polymeren und die Wasserbeständigkeit der metall-katalysierten Filme untersucht.

Die Polymerisiorungsgeschwindigkeits-konstante K wurde für jede der Versuchstemperaturen berechnet; diese Werte wurden mit jenen verglichen, die aus früher publizierten Daten abgeleitet werden konnten. Die Vergleiche ergaben, dass die von uns gefundene Konstante K für, bei 300°C durchgeführte Polymerisationen, innerhalb der in der Literatur angegebenen K-Grenzwerte für in der gleichen Weise polymerisiertes Leinsaatöl lag. Es konnte auch ermittelt werden, dass die Anstrichfilme, die aus bei 300°C polymerisiertem Tabaksamenöl hergestellt worden warensich in ihren Eigenschaften nicht von denen der Leinsaats-

tandölfilme unterschieden. Es wurde fernerhin festgestellt, dass polymerisierte Tabaksamenöl-filme weniger vergilben als Leinsaatölfilme.

3. Vakuum-destillierte Tabaksamenöl-Fettsäuren wurden mit Polyalkoholen wie Pentaerythrit, Sorbit und Tetramethyloyclohexanol verestert und die Eigenschaften der so hergestellten Ester untersucht. Polymere dieser Ester wurden auch hergestellt. Die Trocknungseigenschaften der metall-katalysierten Ester-Monomere und-Polymere und deren Anstrichfilme wurden untersucht. Es ergab sich aus diesem Beobachtungen, dass die Polyalkoholester bessere filmerzugende Eigenschaften hesassen als unmodifiziertes Tabaksamenöl. Die besten Resultate wurden mit Pentaerythrit ester erzielt.

Firnisse wurden auch aus Polyalkoholestern der Tabaksamenöl-Fettsäuren hergestellt und die Eigenschaften der Firnisse untersucht. Die Standhaftigkeit dieser Firniss-filme Wasser und wässerigen Alkali-und Säure-Lösungen gegenüber wurde beobachtet und mit den Eigenschaften der in der gleichen Weise hergestellten Finisses aus polymerisiertem Tabaksamenöls und Leinsaatöls verglichen.

Aus diesen Versuchen und vergleichenden Beobachtungen konnte ermittelt werden, dass Firnisse aus Pentaerythrit Tabaksamenöl-Fettsäuren-estern den Leinsaatöl-Firnissen, die dieselben Kunstharze enthalten, überlegen sind.

4. Tabaksamenöl wurde mit 10 % Maleinsäureanhyrid und mit 10 % Fumarsäure reagiert, und es ergab sich, dass die Additions-Reaktion mit Maleinsäureanhydrid in weniger als 1 Stunde vollendet war, während das Ende der Reaktion mit Fumarsäure nur nach 1, 1/2 stunden erreicht werden konnte.

Mit verschiedenen Polyalkoholen alkoholysiertes (Umesterung) Tabaksamenöl reagierte mit 5 % Maleinsäureanhydrid und Fumarsäure und die so entstandenen Addition Produkte wurden studiert.

Zusammenfassend konnte nachgewiesen werden, dass Tabaksamenöl-Modifikationen mit dibasichen Säuren gute Additions-Produkte ergaben, die zufriedenstellende Eigenschaften hatten.

I. INTRODUCTION.

a). Tobacco seed oil, its properties and economics.

Tobacco seed oil is obtained from the seeds of the tobacco plants *nicotiana tabacum* and *nicotiana rustica* The tobacco is an annual plant mainly growing in America, India, South Africa, Mediterranean countries and Turkey. Tobacco seed is a by-product of tobacco cultivation and the amount of seed is mainly dependent on the type of tobacco produced.

In the cultivation of some types of tobacco no seed can be harvested as a by product since cultivation methods require the removal of the seed heads before they mature, but with certain other types such as, cigar wrapper and Turkish tobaccos surplus seed can be harvested after retaining a small amount for sowing.

The three major tobacco producing zones of Turkey are Aegean Region, Black Sea Region and Marmara Region. The total production of tobacco of Turkey is about 100.000 tons. During the harvesting of most Turkish varieties of tobacco, the seed heads containing approximately 40 % seed. are allowed to remain on the plant. The leaves are removed as they reach the proper stage of development, thus leaving only the stalks and seed heads.

The yield of tobacco seed changes according the type of the plant and the climatic conditions of the cultivation area but in general is 10-15 Kgs. per Dekar in Aegean region and 10 20 Kgs. per Dekar in Black Sea Region. One tobacco plant usually yields 7-28 grs. of seed

The amount of harvested tobacco seed in Turkey is not known, but the area under tobacco cultivation is 156.000 Hectares. Therefore, if harvested, we could expect an approximative yield of 30.000 tons of tobacco seed. But unfortunately 25 % of the tobacco seed is lost to the soil during maturing of the plants and another 20-25 % can not be harvested because of unsuitable climatic conditions in some regions, especially in the Black Sea Region. Therefore 15-20.000 tons of tobacco seed can be taken as being practically available. The amount of tobacco seed available to-day for sale is very small because the cultivators are ignorant of the value of tobacco seed.

Production of other drying oil seeds and semi-drying oil seeds in Turkey is as follows: (1)

Seed	Tonnage for years. 1952	1953	1954
Linseed	22.000	24.000	15.000
Hempseed	5.000	4.000	5.000
Poppyseed	24.000	30.000	6.000
Soybean	3.000	3.000	4.000

Hempseed, poppyseed and soybeans are not processed in Turkey but are generally exported and the only indigenous source of drying oil is linseed, of which 15,000 tons are annually available.

Comparing this figure with the volume of tobacco seed which could easily be made available, the potential importance of the latter becomes apparent. This becomes even more obvious if one considers that tobacco seed oil can be used as an edible product and after hydrogenation could serve as a useful raw material for soap making.

The tobacco seed is very small (1 gr. seed contains approximately 10.000 particules), and due to the primitive ways of harvesting the seed offered for sale is usually mixed with considerable amount of fine sand, earth and tobacco leaf waste. Because of these impurities screw presses cannot be recommended for processing tobacco seed; the fine sand rapidly wears out the main shaft. The seed is therefore generally processed by hydraulic presses or in solvent extraction installations.

The tobacco seed contains 35-42 % of oil which has greenish yellowish colour and dries on exposure to air. Crude tobacco seed oil has a bitter flavour and a characteristic tobacco like smell which can be eliminated by refining processes. In contrast to linseed and soybean oils no break due the decomposition of phosphatides is produced during heating at high temperatures. The chemical and physical characteristics of tobacco seed oil varies according to the species of the plant, climatic conditions of the area in which the plant was grown and the methods of oil extraction. Similar to other seeds, oil obtained from unripe to-

TABLE (1)

The chemical and physical characteristics of tobacco seed oils as found by different investigators.

Source	Density	Refractive Index	Iodine Value	Thiocyanogen Value	Saponification Value	Unsaponifiable %	Acid Value	Viscosity
Kaufmann(2)	0.9230(20°)	1.4762(20°)	135.6					
Mc. Hargue(3)	0.9170(25°)	1.4740(25°)	146.9	—	—	—	—	—
R. Uzac(4)	0.9230(20°)	—	136—143	—	—	1.65	4.3—9.0	—
Narasingaro(5)	0.9105(36°)	1.4600(37°)	112.2	—	—	2.—	0.7	—
Rao(6)	0.9242(25°)	1.4750(26°)	140.7	—	—	0.9	3.9	0.5 poise
Tuğtepe(7)	0.9237(195°)	1.4764(19°)	140—153	—	—	—	1.6—4.12	0.6 poise (24—25°)
Greaves(8)	—	—	140.0	—	—	3.4	—	—
Brambilla(9)	0.9218	1.4775(20°)	132.2(Hubl)				3.2	
	0.9295	1.4789(20°)	128.5(Hubl)	—	—		0.4	
Roberts(10)	0.9240	—	146.7					
	0.9235	—	117.8	—	—	1.25—1.24	2.8	
	0.9175	—	151.6					
Alpar(11)	0.9220(20°)	1.4760(20°)	142.2	—	190.1	2.9	0.93	
	0.9187(20°)	1.4766(20°)	143.0	—	189.5	2.25	8.89	
	0.9231	1.4760(26°)	138.6	—	183.2	1.46	1.55	
Riemenschneider(12)	—	1.4738—42(25°)	139—145	78.3—80.4	—	—	0.3—3.0	
Hilditch(13)	—	1.4742—56	140—145	—	188—190	1.9—2.5	1.6—5.2	
Voerman(14)	0.925	1.4739	142.3	—	190	—	0.5	
The properties of the alkali refined tobacco seed oil used in this research								
	0.923(15°) 0.920(25°)	1.4654(50°)	141.9	—	190.3	—	0.49	21.42 centipoise at 50°C

bacco seed is generally less unsaturated than oil obtained from fully mature seed.

The characteristics of tobacco seed oil obtained from different sources are given in table (1) together with those for the tobacco seed oil used in this research.

The drying properties of tobacco seed oil have attracted the attention of a number of investigators. It is generally classified as semi-drying, although it has also been described as rapidly drying oil, better than linseed oil and useful in varnishes.

Although Greaves$^{(8)}$ states that tobacco seed oil is not a good substitute for linseed oil and will give only by copolymerization with triply conjugated drying oils suitable materials for the coating industry, many other investigators reported that modified tobacco seed oils are as good as linseed oil for making varnishes and paints.

Kaufmann,$^{(2)}$ Balbi$^{(9)}$ and Poinot$^{(15)}$ found it suitable for varnishes. Rao and Ramanaya$^{(16)}$ prepared blown, boiled and polymerized oils from tobacco seed oil and stated that tobacco seed oil is suitable for paint manufacture.

Rao, Mc Grew and Lewis$^{(6)}$ prepared varnishes with ester gum and bakelite GR-284 resin from tobacco seed oil and its alkyds and reported the products suitable for use in decorative paints. Sharma et. al$^{(17)}$ found that tobacco seed oil paints are superior, in respect to their yellowing properties than linseed oil paints. Kapor and Sarin$^{(18)}$ prepared wrinkle finishes from tobacco seed oil for decorative purposes.

In view the confusing and contradictory opinions of the above mentioned investigators an attempt to re-asses the relative value of tobacco seed oil comparing the other oils seemed worth while and its with this aim and view that the present work was undertaken.

b). Improvement and modification methods for the drying and semi-drying oils.

A very minor amount of the drying oils used in the paint and varnishes are not modified and upgraded by some physical or chemical method. Modification or upgrading of the oils used in organic coatings by different methods firstly improve the film forming properties of the oils and secondly secure some specific and desirable characteristics to the films.

Main factors which necessitates the use of modified drying and semi-drying oils in the organic coating industry were summarized by R. L Terril(19) as follows:

1. A war induced shortage of the natural drying oils which has traditionally been employed.
2. The over-all expanding market.
3. Need for better coatings.
4. Desirability for utilization and development of domestic sources of drying oils, and for interchangeability among various oils where necessary.
5. The general advance of research and of applied chemistry

Some of the methods used for the improving and upgrading of drying oils and more especially of semi-drying oils for the above mentioned reasons are given below:

I. Oxidation Polymerization
II. Thermal polymerization
III Esterification of the fatty acids with polyalcohols
IV. Condensation with dibasic acids
V. Co-polymerization with unsaturated hydrocarbons
VI. Segregation to the unsaturated and saturated fractions.
VII. Isomerization and conjugation.
VIII. Interesterification with conjugated drying oils

In this research the first four methods of the above were applied to the alkali refined tobacco seed oil and the results obtained are given.

II EXPERIMENTAL PART.

a). Oxidation Polymerization of tobacco seed oil.

Refined tobacco seed oil was blown at 105, 150 and 195 C° with pure oxygen. Reactions were carried out in a three necked flask equipped with a stirrer and a sampling tube. A slight vacuum was also applied to the outlet of the flask in order to eliminate the reaction products rapidly. Samples withdrawn at irregular intervals were analyzed for viscosity, acid value, peroxide value, density and refractive index. The results obtained are shown in table (2) and in the (figures 1, 2).

The viscosity, acid value, peroxide value, density and refractive index increased with reaction temperature and reaction time but iodine value decreased. Peroxide values rose to a maximum during each blowing experiment and then decreased again. The highest peroxide value were obtained during the blowing at 105 C°.

Tobacco seed oil blown at 105 C° was very much lighter in colour than tobacco seed seed oils blown at 150 and 195 C°.

Table (3) shows the drying times of the final blowing products with different drier compositions. Generally, drying times of the tobacco seed oil films blown at 195 C° are shorter than the drying times of the films from tobacco seed oils blown at 105 and 150 C°. Co and Pb-Mn drier mixtures were found to be the best driers for the oils blown at 195 C°. Co and Co containing drier mixtures were also found suitable for the tobacco seed oil blown at 150 C°. Pb-Mn mixture did not give a good result for the oil blown at 105 C°.

The films of oils blown at 105 and 150 C° were tacky, but the films of tobacco seed oil blown at 195 C° showed less tackiness. The film of tobacco seed oil blown at 195 C° and containing Co as the sole drier proved to be the least tacky. Generally speaking films which contain Co driers were less tacky for each blown oil than the films containing Pb, Mn, and Pb-Mn drier mixtures

The adhesion of the blown oil films to clean tin plates was found to be very good.

TABLE (2)

Results obtained for oxidation polymerization of alkali refined tobacco seed oil with pure oxygen at 105°, 150° and 195° C. Oxygen rate: 30 l/hr.

t C°	Reaction time Hours	Viscosity (c.p.) 50.0 ± 0.1 C°	Iodine Value Wijs	Acid Value MgrKOH/gr	Peroxide Value Mmol/Kg.	Refractive Index 50.0 ± 0.1 C°	Density 25.0 C°
105 ± C°	0	21.42	141.92	0.78	21.06	1.4656	0.920
	1.5	39.41	128.50	1.47	429.49	1.4684	0.934
	3.8	120.3	106.69	5.56	437.68	1.4710	0.960
	5.5	270.8	92.44	7.30	351.85	1.4728	0.976
	7.5	845.3	86.35	11.14	306.38	1.4743	0.990
	9.5	2382.0	77.58	14.39	250.52	1.4752	0.994
150±5C°	0	21.42	141.92	0.70	23.66	1.4658	0.920
	0.5	33.51	131.40	1.68	85.96	1.4674	0.929
	1.25	61.11	123.72	3.58	82.73	1.4691	0.940
	3.25	544.9	92.02	7.63	62.44	1.4738	0.976
	4.75	3159.0	82.56	11.25	11.36	1.4761	0.996
195±1C°	0	21.42	141.92	0.70	19.80	1.4660	0.920
	0.5	36.02	132.63	2.99	39.54	1.4679	0.930
	1.0	62.68	124.01	4.82	36.29	1.4698	0.941
	1.5	130.8	112.98	5.72	17.56	1.4720	0.952
	2.0	274.9	102.17	—	11.90	1.4739	0.964
	2.5	819.1	93.50	8.70	6.00	1.4760	0.975

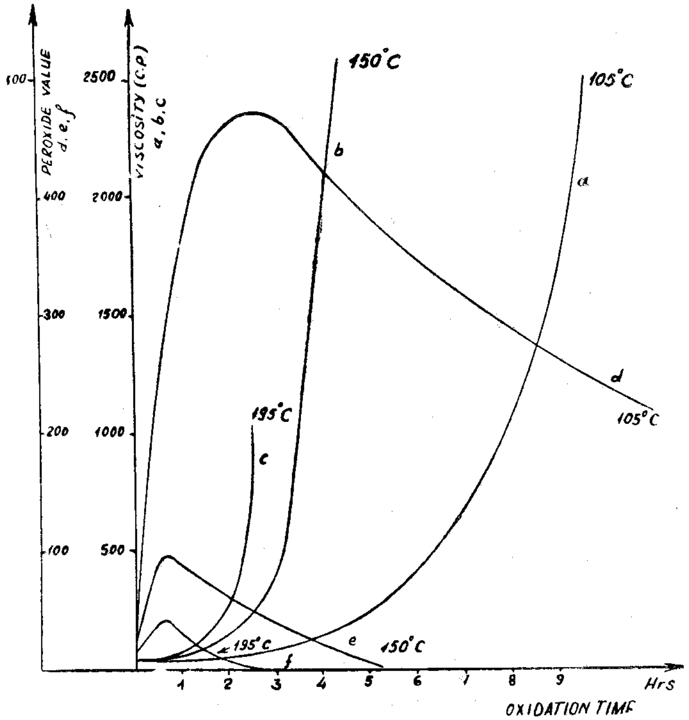

Fig. 1. Viscosity and peroxide value change in the oxidation polymerization of tobacco seed oil.

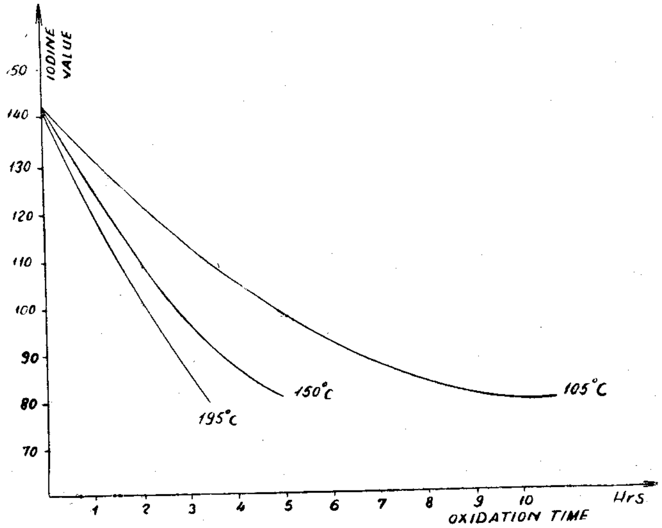

Fig. 2. Iodine Value change in the oxidation polymerization of tobaccosed oil.

TABLE (3)

Drying times of oxidatively polymerized tobacco seed oil films with different drier metals, on glass plates.

Room temperature $= 18 \mp 1$ C
Relative humidity $= 46$ %

Drier Metal %	Drying times (hours)		
	Tobacco seed oil oxidized at 105 C°.	Tobacco seed oil oxidized at 150 C°	Tobacco seed oil oxidized at 195 C°
Co 0.1 %	8.—	4.—	2.5
Mn 0.1 %	24.—	9.—	20.—
Pb 0.2 %	24.—	24.—	24.—
Co 0.1 %+Pb 0.2%	8.—	6.—	2.—
Co 0.1 %+Mn 0.1%	24.—	4.—	4 —
Pb 0.2 %+Mn 0.1%	20.—	4.—	2.—

Water resistance of the blown tobacco seed oil films was also determined by soaking the films in water for 24 hrs.

Films of tobacco seed oils blown at 105 and 150 C° blushed in 2 hours whereas the films of the oil blown at 195 C° started to blush slightly after 10 hours. Table (4) gives the water resistance of the films with different drier compositions. The most water resistant films were those produced from the oil blown at 195 C° and containing Co, Mn and Mn-Pb driers. These films were also the hardest films. Blown tobacco seed oil films were found to be non-resistant to alkaline solutions.

Paint films of blown tobacco seed oils with TiO_2 pigment were slightly tacky but they showed less yellowing than blown linseed oil paint films. The least tacky film between the paint films was again the film of the oil blown at 195 C°.

From the above it seems that the most satisfactory blown tobacco seed oil is the one processed at 195 C°. Its films were found to be rapid drying, little tacky and well water resistant. Blowing at low temperatures is not recommended because of the poor qualities of the films obtained from the oils so treated.

TABLE (4)

Water resistance of the oxidatively polymerized tobacco seed oil films which contain different drier metals.

Air drying time : 96 hours.
Water soaking time: 24 hours.
Water temperature : 18∓2C°

Drier Metal %	Appearence and relative hardness of the films after 24 hrs.							
	Tobacco seed oil oxidized at 105 C°		Tobacco seed oil oxidizet at 150 C°		Tobacco seed oil oxidized at 195 C°		Tobacco seed Oil refined.	
	Appea.	Hardness	Appea.	Hardness	Appea.	Hardness	Appea.	Hardn
Co 0.1 %	b	d	sb	vs	nb	h	b	vs
Mn 0.1 %	b	d	sb	vs	nb	h	b	vs
Pb 0.2 %	b	d	b	vs	vsb	h	b	vs
Co 0.1 % + Mn 0.1 %	b	d	vsb	vs	vsb	h	b	vs
Pb 0.2 % + Mn 0.1 %	b	d	vsb	vs	nb	h	b	vs
Co 0.1 % + Pb 0.2 %	b	d	sb	vs	vsb	h	b	vs

b : Blush sb : Slightly blush vsb : Very slightly blush nb : Non blush
d : Destroyed vs : Very soft film h : Relatively harder than vs

b. Heat polymerization of tobacco seed oil.

1. Literature on heat polymerization of tobacco seed oil.

Heat polymerized tobacco seed oils were prepared by several investigators under various conditions.

Brambilla and Balbi(9) polymerized tobacco seed oil at 297-300 C° and 333-337 C° under the protection of CO_2 atmosphere and with a pressure of 100 mm. Hg. Their results are given in table (5).

Rao and Mc. Grew(6) also prepared stand oils from tobacco seed oil at 260, 300 and 316 C°. Table (6) gives the results of these investigators. Recently M. Tugtepe(7) investigated the characteristics of the heat polymerization of the tobacco seed oil in open vessels under the influence of the atmospheric oxygen.

Sharma, Budhraja and Aggarval(17) prepared double boiled and stand oils from tobacco seed oil. Stand oils were prepared by heating the raw oil at 270-280 C° for 6-7 hrs. double boiled oils were prepared from raw tobacco seed oil also by heating the oil in open pans at 220-235 C° for 8 hrs. According to Sharma et. al (17) the films of double boiled tobacco and stand tobacco seed oils stick as tenaciously to a tin plate as the corresponding linseed oil films. They were resistant to white spirit and carbon tetrachloride while benzene, aceton and ether remove them rapidy. The films of the tobacco seed oil blushed when kept in water for 24 hrs., but regained their original colour after drying in air. The blushing with linseed oil films were permanent. 10 % sulphuric acid had no effect on the films but they dissolve easily within 5 to 10 minutes in 5 % NaOH solution.

2. Results obtained in this research for heat polymerization of tobacco seed oil and their comparisons with findings of previous investigators.

The process of heat polymerization at temperatures of 260, 300 and 320 C° of neutralized tobacco seed oil was investigated Polymerization reactions were carried out under an atmosphere of CO_2 for the elimination of the atmospheric oxygen. Samples

TABLE (5)

Results obtained by Brambilla and Balbi(9) for the heat polymerization of tobacco seed oil at 297-300 C° and 333-337 C° under CO_2 atmosphere.

	297-300 C° Characteristics				337-333 C° Characteristics			
Polymerization Time	Viscosity cp, at 20 C°	n^{20}_D	Acid Value	Iodine Value	Viscosity cp. at 20 C°	n^{20}_D	Acid Value	Iodine Value
30 mins.					193	1.4818	5.6	108.3
60 mins.					1726	1.4862	11.3	73.2
90 mins.					3517	1.4883	14.7	57.4
120 mins.					9363	1.4901	24.2	55.8
150 mins.					47531	1.4954	27.8	47.3
6 hrs.	1280	1.4842	7.5	89.5				
7 hrs.	2027	1.4864	9.3	79.8				
8 hrs.	3848	1.4883	11.4	72.2				

TABLE (6)

Results obtained by Rao, Mc. Grew and Lewis(6) for the heat polymerization of tobacco seed oil at 260, 300 and 316 C° under CO_2 atmosphere.

	260 C°			300 C°			316 C°		
Heating time Hours.	Viscosity cp. at 25 C°	Acid Value	n^{26}_D	Viscosity cp. at 25 C°	Acid Value	n^{26}_D	Viscosity cp. at 25 C°	Acid Value	n^{26}_D
0	50	0.2	1.4748	50	0.3	1.4748	50	0.6	1.4750
1	60	0.4	1.4749	—	2.3	1.4758	135	6.3	1.4770
2	65	0.6	1.4750	120	4.2	1.4768	350	10.8	1.4798
3	73	0.8	1.4751	225	6.0	1.4780	1000	14.2	1.4817
3.5	—	—	—	—	—	—	1500	17.3	1.4826
4	78	1.1	1.4752	400	6.3	1.4757	2500	18.8	1.4830

were withdrawn at irregular intervals and analyzed for viscosity, acid value, iodine value and refractive index. The results obtained are given in table(7)and in figures (3, 4) As it can be seen from figure (4),viscosity increase is proportionally related to the increase of reaction temperature. Although the polymerization time viscosity curve for 260 C° is almost a direct line, the curve for 320 C° is an exponential curve. Increase of iodine value, refractive index and acid value per unit of time also become greater with the increase of the reaction temperature.

TABLE (7)

Results obtained for the heat polymerization of neutralized tobacco seed oil at 260, 300 and 320 C° under carbon dioxide atmosphere.

Polymerization t C°	Heating Time Hours.	Viscosity centi poise 50.0±0.1 C°	Acid Value	Iodine Value (Wijs)	Refractive Index. 50.0±0.1 C°
260 C°	0.—	22.20	0.76	141.92	1.4659
	1.—	22.83	1.30	138.62	1.4660
	2.—	23.45	1.63	137.58	1.4661
	3.—	24.04	1.87	132 93	1.4662
300 C°	0.5	32 68	3.39	136 55	1.4675
	2.—	116.99	7.30	113.45	1.4720
	3.—	202.94	7.61	100 23	1.4733
	4.—	362.40	7.87	94.78	1.4749
320 C°	0.—	23.21	1.20	141.00	1.4663
	0.5	42.97	6.95	126.99	1.4682
	1.—	86.16	10.77	115.61	1.4709
	1.75	271.88	14.95	97.53	1.4741
	2.5	816.24	16.85	91.13	1.4768
	3.—	1721.1	18.88	86.55	1.4781

From the viscosities and the polymerization times polymerization rate constants (K Value) for each temperature were calculated by using the Cannegieter(20) formula. In table (8) the calculated K polymerization rate constants of tobacco seed

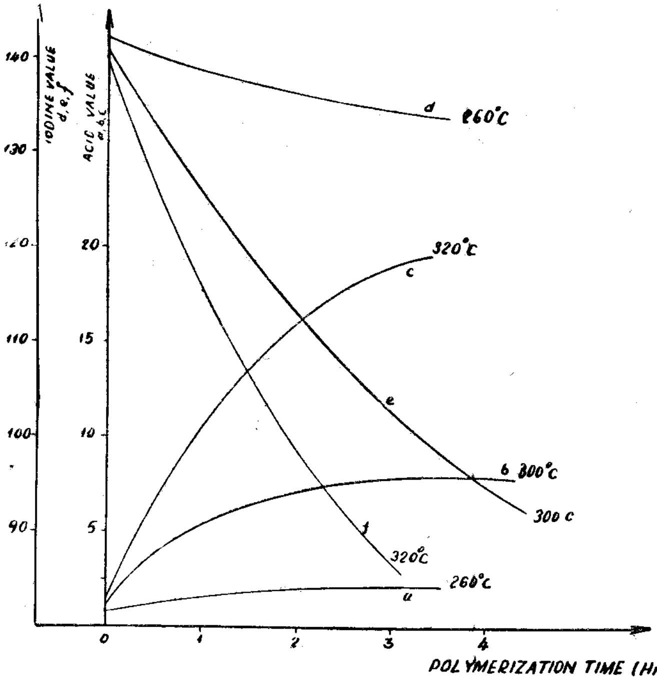

Fig. 3. Acid Value and Iodine Value change in the heat polymerization of tobacco seed oil.

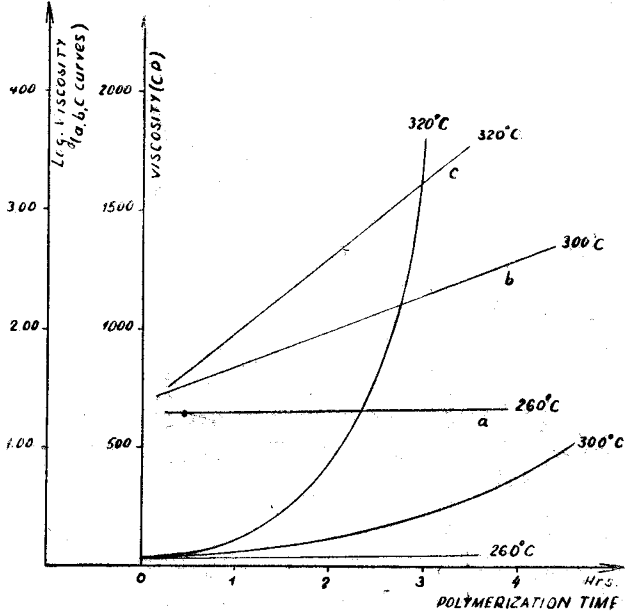

Fig. 4. Viscosity and Log-Viscosity change in the heat polymerization of tobacco seed oil.

oil for each temperature are given and compared with the K constants calculated from the data of **Brambilla** et. al.(9). and Rao et. al.(6) It was not possible to calculate the K polymerization rate constants from the data of M. Tugtepe(7) because the viscosities were given in time units.

Log. Viscosity - polymerization time curves are straight lines with different inclinations, figure (4). As it can be seen from table (8) K value calculated for the heat polymerization at 300 C° is not very different from the K value calculated from the data of other investigators. K value obtained for the polymerization at 260 C° is smaller than the K value calculated from the data of Rao et. al.(6)

It is intresting to note that K values for tobacco seed oil at 260 and 300 C° are within the range of K values for linseed oil given by Cannegieter(23) as being 0.0032 - 0.0057 for 300 C° and 0.0007 for 260 C°. This means that tobacco seed oil is an oil which can polymerize as rapid as linseed oil at 300 C°.

Drying times of the final products with different driers were determined and the results obtained are given in table (9). Co was found to be the best drier metal for the polymerized tobacco seed oils processed at 300 and 320 C°. Co-Mn, Pb-Mn and Pb-Co drier combinations gave shorter drying times for the tobacco seed oil polymerized at 260 C°, than the Co drier alone. Pb and Mn driers did not give good results when used separately, but the mixture of these two metals gave quite good results.

Drying time of the films of the tobacco seed oil polymerized at 300 C° containing Co, Pb, Co-Pb, Mn-Pb driers are shorter than the films of the tobacco seed oils polymerized at 320 and 260 C°, containing the same driers.

Water resistance of the metal catalyzed films was also investigated and the results obtained are given in table (10). The most water resistant films were those produced from the oil polymerized at 300 C° and containing Co, Pb, Co-Pb, and Pb-Mn driers.

Generally the films containing Co and Mn driers separately were found the least water resistant. Films containing Pb drier alone have better water resistance than the films containing

TABLE (8)

The polymerization rate constants of tobacco seed oil for different temperatures calculated by the following Cannegieter formula.

$$K = \frac{\log v - \log v'}{t - t'}$$

where, v and v' are the viscosites in poise at the time of polymerization of t and t' minutes, respectively.

K Values

Temperature C°	From the data of Brambilla and Balbi	From the data of Rao et al.	From the results of this research.
260	—	0.00065	0.00019
297—300	0.00397	—	—
300	—	0.00438	0.00472
316	—	0.00697	—
320	—	—	0.01088
333—237	0.01864	—	—

TABLE (9)

Drying times of the heat polymerized tobacco seed oil films with different drier metals, on glass plates.

Room temperature = 23 ∓ 2 C°
Relative humidity = 59 %

Drying times (hours)

Drier Metal %	Tobacco seed oil polymerized at 260°C	Tobacco seed oil polymerized at 300°C	Tobacco seed oil polymerized at 320°C
Co 0.1 %	8.—	3.—	3.5
Mn 0.1 %	20.—	30.—	32.—
Pb 0.2 %	36.—	30.—	48.—
Co 0.1 % + Mn 0.1%	7.—	10.—	10.—
Co 0.1 % + Pb 0.2%	7.—	3.—	3.5
Pb 0.2 % + Mn 0.1%	7.—	3.—	3.5

TABLE (10)

Water resistance of the heat polymerized tobacco seed oil films which contain different drier metals.

Air drying time = 96 hrs.
Water soaking time = 24 hrs.
Water temperature = 18 ∓ 3 C°.

Drier Metal %	Appearence and relative hardness of the films after 24 hrs.							
	Tobacco seed oil polymerized at 260 C°		Tobacco seed oil polymerized at 300 C°		Tobacco seed oil polymerized at 320 C°		Tobacco seed Oil Neutralized	
	Appea.	Hardness	Appea.	Hardness	Appea.	Hardness	Appea.	Hardness
Co 0.1 %	b	vs	sb	vs	sb	vs	b	vs
Mn 0.1 %	b	vs	sb	vs	b	vs	b	vs
Pb 0 2 %	sb	vs	vsb	h	sb	vs	b	vs
Co 0.1 % + Mn 0.1 %	b	vs	sb	h	b	vs	b	vs
Mn 0.1 % + Pb 0.2 %	b	vs	vsb	h	sb	vs	b	vs
Co 0.1 % + Pb 0.2 %	b	vs	vsb	h	sb	vs	b	vs

b: Blush sb: Slightly blush vsb: Very slightly blush nb: Non blush
d: Destroyed vs: Very soft film h: Relatively harder than (vs).

other driers. All the films regained their original appearence after 3-5 hrs. keeping in the air.

In order to investigate the behaviour of tobacco seed oil in paints, a paint was prepared from the tobacco seed oil polymerized at 300 C° and TiO_2 pigment; and this paint was compared with a heat polymerized linseed oil paint prepared similarly.

The paint films applied on clean iron sheets and were exposed to the atmospheric conditions over a period of 2 years. Although the tobacco seed oil paint film showed a little tackiness at the beginning, this tackiness dissapeared in 15 days. The condition of the films after 2 years was exactly the same and none of the films showed any deterioration.

As a result of the above mentioned investigations it is possible to state that heat polymerized tobacco seed oil has better film forming properties than the tobacco seed oil. The films of the heat polymerized tobacco seed oils are quicker drying and considerably resistant to water. 300 C° was found to be the best polymerization temperature. The films of the tobacco seed oil polymerized at 300 C° are more rapid drying and more water resistant than the films of the tobacco seed oils polymerized at 260 and 320 C°.

The durabilitiy of paint films prepared from the tobacco seed oil polymerized at 300 C° was found to be same as the durability of a linseed stand oil paint films prepared similarly. This shows us that the polymerized tobacco seed oil can replace linseed stand oil in oil paints without any difficulty. Polymerized tobacco seed oil can also be used in varnish manufacture. (see c-2).

c. Esterification of tobacco seed oil fatty acids with polyalcohols

1. Pentaerythritol, tetramethylolcyclohexanol and sorbitol esters of tobacco seed oil fatty acids. Their characteristics and film forming properties.

Vacuum distilled tobacco seed oil fatty acids were esterified with pentaerythritol (P.E.), tetramethylolcyclohexanol (T.M.C.)

and sorbitol. The esterifications were carried out under an CO_2 atmosphere and at temperatures of 240-250 C° (see experimental part). For the esterification of P.E. and sorbitol no catalyst was used, but zinc stearate was employed as catalyst for the esterification of T.M.C. An excess of 10 % of polyalcohols were used over theory.

The polyalcohol esters obtained were analyzed for viscosity, acid value, refractive index and colour. Drying time, water resistance and adhesion properties of the ester films were also investigated.

Bodied esters were prepared by heating the fatty acid esters under a CO_2 atmosphere at the temperatures of 295 ∓ 10 C°, for three hours and the above mentioned properties were also determined for the bodied esters.

Results obtained are shown in table (11), where they are compared with both neutralized and bodied tobacco seed oil. As it can be seen from table (11) P.E. ester and its bodied form was lighter in colour than the other esters and their bodied forms. The darkest in colour was the T.M.C. ester and its bodied form. Acid values of the sorbitol ester and tobacco seed oil (i. e glycerol ester) increased during bodying, whereas acid values of the P.E. and T.M.C. esters decreased. This unusual fact can be explained that the during the bodying process at high temperature, esterification of the fatty acids continued. Although the viscosities of the P. E. ester and tobacco seed oil bodied forms are the same, acid value of the former is comparatively smaller. Sorbitol and glycerol esters showed approximately the same viscosity increase, which is 4.5 times of their initial viscosity. Viscosity increase of the P.E. and T.M.C. esters were 2.5 and 3.1 times of their initial viscosities respectively.

Drying times of the tobacco seed oil fatty acid esters are shown in table (12) for different drier compositions. Bodying of the esters generally decrease the drying times as can be expected. The most rapidly drying unbodied ester is the T.M.C. ester which contains 0.1 % Co as drier metal. After heat polymerization of the P. E., T.M.C. and sorbitol esters the drying times with 0.1 % Co were found to be nearly the same.

Films produced by bodied and unbodied tobacco seed oil were all. tacky, sorbitol ester were slightly so, but P. E. and

TABLE (11)

Properties of the P.E., T.M.C., and sorbitol esters of tobacco seed oil fatty acids and their bodied forms.

	P. E. Ester		T. M. C. Ester		Sorbitol Ester		Tobaccosed Oil	
Properties	Normal	Bodied 3 hrs. at 295 C°	Normal	Bodied 3 hrs at 295 C°	Normal	Bodied 3 hrs. at 295 C°	Normal	Bodied 3 hrs. at 295 C°
Viscosity (c. s.) at 50.0∓01 C°	37.50	94.86	65.96	207.40	55.01	247.52	22.57	95.54
Acid Value	5.25	2.51	27.36	23.89	6.89	18.59	0.82	5.89
Colour Lovibond 1 inch cell Yellow-Red	10—1	20—3.1	50—6.0	70—17	20—3	55—17	50—1.3	50—9,5
Refractive Index at 50.0∓0.1 C°	1.4689	1.4719	1.4755	1.4790	1.4710	1.4750	1.4658	1.4710

TABLE (12)

Drying times of tobacco seed oil fatty acids P.E., T. M. C. & sorbitol esters and tobacco seed oil with different drier compositions on glass plates.

Room temperature = 24 C°
Relative Humidity = 56 %

Drier metal %	Drying times (hours).							
	P. E. Ester		T. M. C. Ester		Sorbitol Ester		Tobacco seed oil	
	Normal	Bodied	Normal	Bodied	Normal	Bodied	Normal	Bodied
Co0.1 %	4.—	2.5	2.—	2.5	3.—	2.5	4.—	4.—
Mn0.1 %	7.—	22.—	20.—	22.—	48.—	24.—	48.—	36.—
Pb 0.1 %	20.—	18.—	20.—	18.—	48.—	36.—	48.—	20.—
Co 0.1 % + Mn 0.1%	10.—	4.—	5.5	5.—	3.—	4.—	4.—	5.—
Co 0.1 % + Pb 0.1%	4.—	3.—	3.—	3.—	3.—	2..5	4.—	4.—

T.M C. ester films were not. The adhesion of the films to clean tin plates was found very good for all esters.

Water resistance of the films was also investigated and it was found that P.E. ester films which contain Mn driers did not produce blushing after 24 hrs. soaking in water. P.E. ester films which contain Co, Co-Pb, and Pb driers were blushed very slightly after similar treatment. Table (13) shows the results obtained from the water soaking tests. Films produced from tobacco seed oil blushed most and it was easy to remove them from glass plates by slight rubbing. In general the films which contain Pb and Mn as drier were more water resistant than the films which contain Co as drier. After removing the films from water, they regained their initial appearence after drying for 3-4 hrs. in air.

Paints of the bodied esters with TiO_2 pigment were prepared with different drier compositions. Drying times of the paint films were nearly the same as the bodied esters for the same catalyst composition Films examined 1 month after they had become dry showed that P.E. and T.M.C. ester paint films were not tacky but tobacco seed oil and to a much lesser degree sorbitol ester films were tacky. The most tacky film was found to be the film of bodied tobacco seed oil paint which contain only Co as drier.

As a result of the above experiments it is possible to state that esterification of tobacco seed oil fatty acids with P.E. T.M.C. and sorbitol give improved drying oils, which have shorter drying times, produce non tacky and more water resistant films than the tobacco seed oil.

2. Varnishes from tobacco seed oil fatty acids polyalcohol esters and their comparison with those prepared from heat polymerized tobacco seed and linseed oils.

Varnishes from tobacco seed oil fatty acids P. E., T. M. C. and sorbitol esters and from polymerized linseed and tobacco seed oils were prepared. Resins used for the varnishes prepared from polymerized linseed and tobacco seed oils were Bedesol 33 phenolic resin from I C. I and a Maleic resin of German origin which is a rosin maleic anhydride adduct. For the var-

TABLE (13)

Water resistance of the tobacco seed oil fatty acids P. E., T. M. C. and sorbitol ester films which contain different driers.

Water soaking time = 24 hrs.
Water temperature = 23 C°

Drier metal %	Appearence of the films after 24 hrs.							
	P. E. Ester		T. M. C. Ester		Sorbitol Ester		Tobacco seed Oil	
	Normal	Bodied	Normal	Bodied	Normal	Bodied	Normal	Bodied
Co 0.1 %	b	sb	b	b	b	b	b	b
Mn 0.1 %	sb	n	b	vsb	sb	vsb	b	b
Pb 0.1 %	sb	vsb	b	sb	sb	sb	b	sb
Co 0.1 % + Mn 0.1%	b	n	b	sb	b	sb	b	b
Co 0.1 % + Pb 0.1%	b	sb	b	b	b	b	b	b

b: Blush   sb: Slightly blush   vsb: Very slightly blush   nb: Non blush.

nishes from the P. E, T. M. C. and Sorbitol esters only Bedesol 33 resin was used.

The composition of the varnishes were as follows:

Resin	20.0 gr.
Oil or ester	25.0 gr.
White spirit	55.0 ml.
Co (as naphtenate)	0.01 gr.
Pb (as naphtenate)	0.1 gr.

According to the above composition these varnishes are in the class of medium oil length (13), hard drying flatting varnishes. (For preparation of the varnishes see experimental part).

TABLE (14)

Properties and drying time of the varnishes prepared from polymerized tobacco seed oil fatty acid esters, heat polymerized tobacco seed oil and heat polymerized linseed oil.

Varnish	Colour (Lovibond) 1 inch cell		Acid Value	Drying Time	
	Yellow	Red		Set to touch Hrs.	Hard Dry Hrs.
Linseed oil-Bedesol 33 Resin	75	26	5.44	2.5	6.—
Linseed oil-Maleic Resin	20	9	6.91	2.5	6.—
Tobaccoseed oil-Bedesol 33 Resin	55	23	7.58	2.—	6.—
Tobaccoseed oil-Maleic Resin	55	13	6.75	2.5	6.—
P. E. ester-Bedesol 33 Resin	50	21	5.38	2.5	7.—
T. M. C. ester-Bedesol 33 Resin	70	28	9.80	3.—	9.5
Sorbitol ester-Bedesol 33 Resin	70	35	9.08	3.5	9.5

The properties of the varnishes are given in table (14). As it is seen from the table maleic resin varnishes are lighter in colour than the Bedesol varnishes. Tobacco seed oil-maleic resin varnish is darker in colour than linseed oil-maleic resin varnish but there is no difference between their drying times. Among

TABLE (15)

Water resistance of the varnish films prepared from polymerized tobacco seed oil fatty acids esters, heat polymerized tobacco seed oil and heat polymerized linseed oil.

Air Drying time = 48 hrs.
Water soaking time = 24 and 48 hrs.
Water temperature = 28 ∓ 2 C°

Varnish	Appearence after 24 hrs.	Appearence after 48 hrs.
Linseed oil-Bedesol 33 Resin	vsb	vsb
Linseed oil-maleic Resin	sb	b
Tobacco seed oil-Bedesol 33 Resin	vsb	sb
Tobacco seed oil-Maleic Resin	sb	b
P. E. Ester-Bedesol 33 Resin	nb	nb
T. M. C Ester-Bedesol 33 Resin	vsb	sb
Sorbitol Ester-Bedesol 33 Resin.	sb	b

b: Blush vsb: Very slightly blush sb: Slightly blush
nb: Non blush.

the Bedesol resin varnishes the P.E. ester varnish is lightest in colour and has the smallest acid value. The drying times of the films of tobacco seed oil-Bedesol resin varnish is very close to those for linseed oil-Bedesol varnish films. T. M. C. and sorbitol ester-Bedesol varnishes are dark in colour and have relatively longer drying times than the other Bedesol varnishes.

Resistance of the varnish films to water, aqueous alkaline and acid solutions were also determined by soaking the films in water, N/10 NaOH solution and 5 % acetic acid solution after keeping them in air for 48 hous. The results obtained are given in tables (15, 16).

In general Bedesol varnishes are more water resistant than Maleic resin varnishes films. The most water resistant varnish film was found to be the one from P. E. ester-Bedesol varnish. Even after keeping it in water for 48 hours this film did not show any change or blushing. Tobacco seed oil-Maleic resin varnish films were found to be the least resistant to alkaline solution. The most resistant film to alkaline solution, is the one obtained from P. E. ester-Bedesol varnish. The resistance of this film is greater than that for linseed oil-Bedesol varnish film. (see table 16).

The resistance of the varnish films to acid solutions was investigated by soaking the films into an aqueous 5 % acetic acid solution for 24 hours. All the films showed different degrees of blushing but again the P. E. ester-Bedesol varnish film was found to be the most resistant.

None of the films of the varnishes are brittle and their adhesion to tin plates is very good. Varnish films applied on wood panels and kept indoors for 2.5 years are still in perfect condition.

It can be stated that tobacco seed oil and tobacco seed oil fatty acids-polyalcohol esters are suitable materials for varnishes There is not a big difference between the varnishes prepared with polymerized tobacco seed oil and those prepared from polymerized linseed oil. The best varnish was found to be the tobacco seed oil fatty acids penta erythritol ester-Bedesol 33 varnish. This varnish has a number of more desirable properties than the linseed oil-Bedesol resin varnish.

TABLE (16)

Alkali and acid resistance of the varnish films prepared from polymerized tobacco seed oil fatty acids esters, heat polymerized tobacco seed oil and heat polymerized linseed oil.

Air drying time = 48 hrs.
Temperature of the N/10 NaOH solution = 28 ∓ 1 C°
Temperature of the 5 % CH_3COOH solution = 28 ∓ 1 C°.

Varnish	Acid	Alkaline
	Appearence of the films after 24 hrs. soaking	Time required for destruction of the films. Hours.
Linseed oil-Bedesol 33 Resin	sb	7.—
Linseed oil-Maleic Resin	sb	4.5
Tobacco seed oil-Bedesol 33 Resin	b	4.5
Tobacco seed oil-Maleic Resin	b	3.—
P. E. Ester-Bedesol 33 Resin	vsb	8.5
T. M. C. Ester-Bedesol 33 Resin	b	5.—
Sorbitol Ester-Bedesol 33 Resin	sb	4.5

d. Modification of the tobacco seed oil with maleic anhydride and fumaric acid.

The addition reactions of tobacco seed oil with maleic anhydride and fumaric acid were investigated by reacting the neutralized tobacco seed oil with the acids. To esterify free carboxyl groups of the adducts, different polyalcohols were used.

Neutralized tobacco seed oil, containing 10 % of its weight maleic anhydride or fumaric acid, was heated at 260 C° under a CO_2 atmosphere. Samples withdrawn at half an hour intervals were washed several times with hot distilled water, until the wash waters did not show acid reaction, and dried under vacuum. The acid value of the sample was then determined. The results obtained are given in table (17).

TABLE (17)

Acid value increase during the addition reaction of tobacco seed oil with 10 % maleic anhydride and fumaric acid.

Reaction Time at 260 C° Hour.	Acid Value 10 % maleic anhydride	 % 10 fumaric acid
0	42.80	10.18
0.5	55.35	35.29
1.0	55.05	—
1.5	55.75	61.47
2.5	—	61.54

Acid values indicated that the addition reaction between tobacco seed oil and fumaric acid was completed in 2 hours, whereas the reaction with maleic anhydride took less than 1 hour, figure (5).

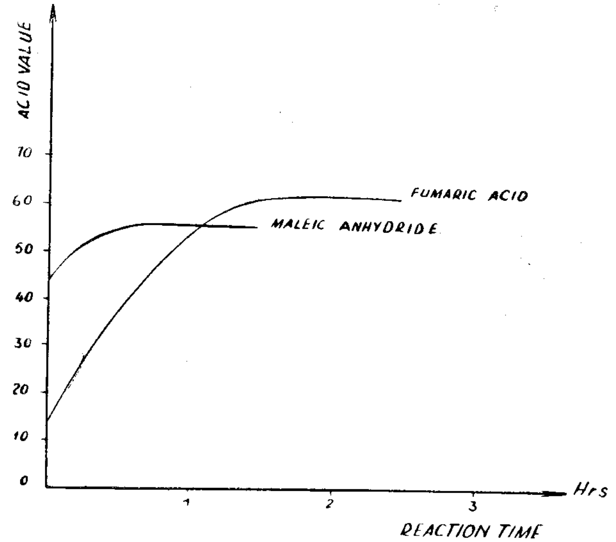

Fig. (5). Acid value increase in the addition reaction of tobacco seed oil with maleic anhydride and fumaric acid.

Acid values of the adducts were found to be less than half of the expected theoretical acid value. This fact was also reported by other investigators for the reaction of these diacids with other vegetable oils.(21)

For esterification the free carboxyl groups of the adducts, which contain 10 % diacids, were heated with the theoretical amount of poly alcohols at 260 C° for 1 hour. When the temperature increased to 290-300 C° for polymerization, all the reaction mixtures gelled in a very short time, e g. 5 to 10 minutes. Conclusion obtained from this is that the addition of 10 % diacids to tobacco seed oil increases the reactivity too much.

Taking the results given above into the consideration, the method of the esterification and the amount of the dibasic acids changed. Tobacco seed oil first alcoholyzed with polyalcohols (pentaerythritol, α methyl glucoside and sorbitol) and the resulting esters containing hydroxyl groups reacted with maleic anhydride and fumaric acid. The amounts were so arranged that the amount of diacids used was 5 % of the tobacco seed oil. For the preparation of the alcoholyzed tobacco seed oils and their esterification with diacids see experimental part.

The adducts so obtained were analyzed for viscosity, colour, acid value and their gelation time was determined.

The results obtained are given in table (18). As is seen from table (18) the highest viscosity increase for the maleic modified tobacco seed oils was obtained with the tobacco seed oil alcoholyzed with α methyl glucoside. This also had the lightest colour and lowest acid value. The fumaric acid adducts showed smaller increases in viscosities than maleic anhydride adducts as expected. It has been reported many times that fumaric acid is not as active as its cis isomer, and this fact becomes more apparent when the gelation time of the fumaric and maleic acid adduct is compared. Generally the gelation time of the fumaric acid adducts is longer than those for maleic anhydride adducts. In both cases adducts obtained from P. E. alcoholyzed tobacco seed oil gelled quicker than all the other adducts. Sorbitol alcoholyzed adducts had the longest gelation time The effects of poly alcohols is more clearly seen when the gelation times of P. E. - fumaric acid adduct and α methyl glucoside-fumaric acid adduct are compared with the gelation time of the sorbitol-maleic anhydride adduct.

Gelation time of a tobacco seed oil polymerized at 300 C° for 4 hours (viscosity 362.4 cp at 50.0 ∓ 0.1 C°) was also determined and found to be 50 minutes. Taking into account that this heat polymerized tobacco seed oil was kept at 300 C° for 4 hours prior to gelation test, and that the polyalcohol dibasic acid adducts were heated to temperatures in the region of 300 C° for at least 3 hours during their preparation, 110 minutes should be taken as the real gelation time for the heat polymerized tobacco seed oil. This figure is many times higher than the gelation time of the poly alcohol-diacid adducts, a fact which proves that the activity of tobacco seed oil is increased many times by the treatment with polyalcohols and diacids.

Fumaric acid adducts are lighter in colour than the maleic anhydride adducts. In the case of α methyl glucoside alcoholyzed tobacco seed oil this difference is more clearly seen. Sorbitol and P. E. alcoholyzed adducts are lighter in colour than the α methyl glucoside adduts but there is not much difference between their own colours.

Drying time of the adducts, which contain differen drier metals was also determined and the results obtained are given in table (19).

TABLE (18)

Characteristics of the adducts obtained from the reaction of maleic anhydride and fumaric acid with the tobacco seed oils alcoholyzed with different polyalcohols.

Maleic anhydride and fumaric acid : 5 % of the tobacco seed oil by weight.

Maleic anhydride adducts

		Characteristics			
Polyalcohol	Amount of polyacohol added to 100 gr of the tobacco seed oil	Viscosity cp at 50 C°	Acid Value	Colour Lovibond *r* — *y*	Gelation Time at 300 ∓ 5 C°
Pentaerythritol	3.47	234.6	9.80	38—5.7	30 mins.
Sorbitol	4.64	123.0	10.95	20—4.4	60 mins.
α-Methyl glucoside	4.94	335.9	6.58	178—20	40 mins.
		Fumaric acid adducts			
Pentaerythritol	3.93	192.1	6.92	15—3.5	45 mins.
Sorbitol	3.92	76.5	17.81	50—3	60 mins.
α-Methyl-glucoside	4.17	160.8	8.62	70—9.4	55 mins.

TABLE (19)

Drying times of the polyalcoholyzed tobacco seed oil maleic and fumaric acid adduct films with different drier metals, on glass plates

Room temperature : 25—26 C°
Relative humidity : 55 %

Drier Metal %	Drying times (hours)					
	Pentaerythritol		Sorbitol		Methyl glucoside	
	Maleic 5 %	Fumaric 5 %	Maleic 5 %	Fumaric 5 %	Maleic 5 %	Fumaric 5 %
Co 0.1 %	2.—	2.—	3.—	2.5	2.—	2.75
Mn 0.1 %	14.—	13.5	15.5	15.—	8.5	15.—
Pb 0.2 %	48.—	45.—	48.—	45.—	26.—	45.—
Co 0.1 % + Mn 0.1 %	6.—	4.5	6.5	6.5	4.5	5.—
Co 0.1 % + Pb 0.2 %	2.—	2.—	3.—	2.5	2.—	2.75
Pb 0.2 % + Mn 0.1 %	6.—	4.5	11.5	9.—	4.—	6.5

TABLE (20)

Water resistance of the polyalcoholyzed tobacco seed oil-maleic anhydride and fumaric acid adduct films with different drier metals, on glass plates.

Air drying time : 48 hrs.
Water soaping time : 24 hrs.
Water temperature : 24—26 C°.

Appearence of the films after 24 hrs.

Drier Metal %	Pentaerythritol		Sorbitol		α Methyl glucoside	
	Maleic 5 %	Fumaric 5 %	Maleic 5 %	Fumaric 5 %	Maleic 5 %	Fumaric 5 %
Co 0.1 %	vsb	sb	b	b	vsb	sb
Mn 0.1 %	nb	nb	sb	vsb	nb	sb
Pb 0.2 %	nb	nb	sb	vsb	nb	nb
Co 0.1 % + Mn 0.1 %	vsb	nb	sb	nb	nb	vsb
Co 0.1 % + Pb 0.2 %	vsb	nb	b	b	nb	vsb
Pb 0.2 % + Mn 0.1 %	vsb	nb	sb	sb	vsb	vsb

The α methyl glucoside alcoholyzed tobacco seed oil maleic anhydride adduct is the quickest drying of all the maleic adducts, whereas, among tbe fumaric acid adducts P. E. alcoholyzed tobacco seed oil-fumaric acid adduct was found to be the quickest drying.

Fumaric acid added alcoholyzed tobacco seed oils, except the one alcoholyzed with α methyl glucoside, were found to be quicker drying than the corresponding maleic anhydride added alcoholyzed tobacco seed oils.

Co and Co-Pb were found as the most effective driers. Pb and Mn did not give satisfactory results, especially when used separately.

To determine the relative water resistance of the adduct films which contain different dries, after being kept in air for 48 hours, were soaked in water and kept for 24 hours. The results obtained are given in table (20)

Films obtained from modified tobacco seed oils alcoholyzed with P. E and α methyl glucoside were found to be more water resistant than the sorbitol alcoholyzed oils. The most water resistant films were the P. E. - fumaric acid and α methyl glucoside-maleic anhydride modified tobacco seed oil films. Films containing Co drier as the sole drier are less water resistant than those which contain Mn and Pb.

In summing up, therefore, it is found that the adducts formed from fumaric acid and maleic anhydride and penta erythritol, sorbitol and α methyl glucoside alcoholyzed tobacco seed oils have better polymerization characteristics than the tobacco seed oil and the films of these adducts have upgraded drying properties.

This method of modification is suitable for obtaining, quickly, from tobacco seed oils, high viscosity products which also have better film forming characteristics. The penta erythritol and α methyl glucoside alcoholyzed tobacco seed oils produced better products than the sorbitol alcoholyzed tobacco seed oil.

e) Methods of analysis and preparation methods.

1. Acid value :

American Oil Chemists Society (AOCS) (32) standard Ka 2-47 method is used.

2. Iodine Value :

AOCS standard Ka 9-51 method which is based on Wijs method is used.

3. Viscosity :

Viscosity determinations of the oxidation polymerization products were made with the Höppler falling sphere viscosimeter at 50.0 ∓ 0.1 C°.

All the other viscosity determinations were made by a calibrated Ostwald No 3 viscosimeter at 50.0 ∓ 0.1 C°. All the results except those for tobacco seed oil fatty acids poly alcohol esters are given in centi poise units.

4. Peroxide value :

A simplified Wheeler method is used(23), and the peroxide values were calculated as mili mols peroxides per Kgr of oil.

5. Refractive Index :

Refractive indexes were measured by an Abbé-Zeiss refractometer at 50.0 ∓ 0.1 C°.

6. Colour :

Colour determinations were made by a Lovibond tintometer which is equipped with red and yellow colour slides. One inch cells were always used to obtain comparative results.

7. Gelation time :

Gelation times were determined by heating 25 ml of the material in a 100 ml. beaker on an electric heater at 300 ∓ 5 C°. The contents of the beakers were mixed occasionally and the time, in minutes, for complete gelling is recorded.

8. Drying time :

Drying time of the all products were determined as follows : After incorporating the indicated amount of driers as cobalt lead and manganese naphtenates from a concentrated stock solution in white spirit, the products were heated to 150 C° to ensure complete mixing. After keeping the oils two days in closed vessels films were spread on clean glass plates. The glass plates kept at 45 degrees inclination under indirect light and the touch dry and hard dry points of the films were determined by touching with hand and with a cloth respectively.

9. Water resistance of the films :

Dried oil films on glass plates were dipped in water for 24 hours and the degree of blushing recorded.

Similarly the resistance of the varnish films of tobacco seed oil fatty acid poly alcohol esters to acid and alkaline solutions were determined by soaking them in 5 % acetic acid solution and N/10 KOH solution respectively.

b. Preparation methods.

1. Preparation of tobacco seed oil fatty acids.

250 grs neutralized tobacco seed oil was saponified completely by refluxing 3 hours in a three necked flask with 150 gr KOH, 250 grs ethyl alcohol and 100 ml, water. The soap paste obtained is dissolved in 2 lts of water and the solution is decomposed with HCl The mixture was kept at 80—90 C° for complete separation, upper fatty acid layer separated by the aid of a separating funnel is washed three times with hot distilled water and dried with anhydrous Na_2SO_4. Finally crude fatty acids distilled under vacuum at 9 mm. Hg pressure.

2. Esterification of tobacco seed oil fatty acids with polyalcohols.

Esterification processes were carried out in a three necked flask equipped with a stirrer, a thermometer and inlets and outlets for CO_2. The amount of polyalcohols used were as follws, an excess of 10 % of polyalcohols were used over theory.

12.9 grs. pentaerythritol
16 8 grs. T. M. C.
17.5 grs. Sorbitol
} for 100 grs. fatty acids.

Zinc stearate is used as a catalyst (1 gr.) in the esterification with sorbitol.

The end products were heat polymerized at 295 C° for 3 hours under an atmosphere of CO_2.

3. Preparation of tobacco seed oil fatty acid-polyalcohol ester varnishes.

The composition of the varnishes were as follows:

Resin	20 grs.
Oil pr ester	25 gr.
White spirit	55 ml.
Co (as naphtenate)	0.01 %
Pb (as naphtenate)	0.1 %

The resin is heated in a beaker together with the oil to 300 C° and held at that temperature 10 minutes for the oils and 30 minutes for the esters. After cooling to 180 C°, 55 ml white spirit which contains the driers was added.

The determinations and analyses were carried out after keeping the clear varnishes one week at room temperature.

After one year storage only P. E. ester varnish shoved a thin skin on the surface.

4. Modification of tobacco seed oil with maleic anhydride and fumaric acid.

225 grs of neutralized tobacco seed oil and 25 grs. di acid is heated to 260 C° in a three necked flask, equipped with a stirrer. The reaction mixture is held at 260 C° and the samples withdrawn at irregular intervals. The samples were washed with hot distilled water until the wash waters do not give acid reaction to litmus paper. After drying the samples at 110 C°, the analysis were carried out.

5. Esterification of alcoholyzed tobacco seed oil with maleic anhydride and fumaric acid.

150 grs. of neutralized tobacco seed oil is reacted with polyalcohols in a three necked glass flask at 280 C°. The reaction time was approximately one hour. The amount of the polyalcohols were calculated on the maleic and fumaric acid (5 % on weight of the oil) which will be reacted with the alcoholyzed oil. The amounts were as follows :

	P E	Sorbitol	α Me.Glucosid
For 5 grs. maleic anhydride	3.47 gr.	4.64 gr.	4.94 gr.
For 5 grs. fumaric acid	2.93 gr.	3.92 gr.	4.17 gr.

After one hour of reaction with polyalcohol, 7 5 grs maleic anhydride or fumaric acid was added to the reaction mixture and heating continued another hour with constant stirring, the final polymerization was made by heating the reaction mixture another 1 hr at 300 C°. All these reactions were carried out under a CO_2 atmosphere in order to eliminate the effect of atmospheric oxygen.

The content of the flask cooled down to 120 °C and filtered, and the analysis were carried out.

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