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Solvent retention in phenolic varnish films

By M. Yaseen and H. E. Ashton

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Summary

When coatings are air-dried, small amounts of solvent are retained in the film because drying takes place most rapidly at the surface. Hence, coatings that dry the fastest trap the most solvent, and evacuation, even at high vacuum, does not remove all the retained solvent. Removal is accomplished only after several cycles of water absorption and desorption.

The amount of solvent trapped in oil-modified coatings is probably not large enough to have much effect on the physical properties of coatings. When the total solvent removed by both evacuation and desorption is calculated on the basis of the air-dried film weight, 15- and 20-gal tung oil phenolic varnishes contained 0.91 and 1.04 per cent solvent, respectively. This is much lower than the quantities retained in cellulose nitrate and vinyl lacquers. The slowest drying varnish tested, 40-gal dehydrated castor, retained 0.56 per cent solvent.

The amount, however, is sufficient to change drastically the water absorption values obtained when precise measurements are made on coatings that do not absorb much water. This effect will be discussed in detail in a second paper concerned with clear coatings for exterior wood.

Keywords

Types and classes of coating
phenolic varnish

Process and methods primarily associated with analysis measurement and testing

Properties, characteristics and conditions primarily associated with dried or cured films
solvent retention

gas chromatography
infra-red spectroscopy

La rétention de solvant aux feuil de vernis phénolique

Résumé

Pendant le séchage à l'air des revêtements, de petites quantités de solvant sont retenues dans le feuil, puisque le séchage se produit plus rapidement à la surface. Par conséquent des revêtements qui séchent le plus rapidement, attrapent le plus de solvant, et l'évacuation, même sous vide poussé, n'enlève pas tout le solvant retenu. L'enlèvement ne s'accomplit qu'après plusieurs cycles d'absorption d'eau suivi par désorption.

La quantité de solvant attrapée en revêtements modifiés par huile n'est pas probablement assez important d'exercer beaucoup d'influence sur les propriétés physiques des revêtements. Lorsqu'on calcule la quantité totale de solvant enlevée à la fois par évacuation et désorption, et basée sur le poids du feuil sec, des vernis phénoliques de longueur en huile de 15 et de 20 gallon contiennent respectivement de 0,91 et 1,04 pour cent de solvant. C'est beaucoup moins que les c'est quantités retenues par des peintures à base de nitrocellulose ou vinyliques. Parmi les vernis examinés, celui qui sèche le moins vite, de longueur en huile de ricin déshydratée de 40 gallon, retenait de 0,56 pour cent de solvant.

Pourtant, cette quantité est suffisante pour changer gravement les chiffres d'absorption d'eau mis en évidence par des mesures précises effectuées sur des revêtements qui n'absorbent pas beaucoup d'eau. On discutera cet effet au cours d'un exposé subséquent ou l'on considèrera des revêtements clairs pour la boiserie à l'extérieure.

Lösungsmittelretention in Filmen von Phenolharzlacken

Zusammenfassung

Bei Lufttrocknung von Lacken werden geringe Lösungsmittelmengen im Film zurückbehalten, weil Trocknung am schnellsten an der Oberfläche vor sich geht. Daher fangen solche Anstrichmittel, die am schnellsten trocknen, die grösste Menge Lösungsmittel ein, und Entlüftung, selbst unter hohem Vakuum, beseitigt zurückgehaltenes Lösungsmittel nur unvollständig. Die völlige Entfernung wird lediglich nach wiederholten Zyklen von Wasserabsorption und -Desorption ermöglicht.

Bei ölmodifizierten Lacken ist die Menge zurückgehaltenen Lösungsmittels wahrscheinlich nicht gross genug, um die physikalischen Eigenschaften derselben wesentlich zu beeinflussen. Berechnet auf Grund des luftgetrockneten Filmgewichtes enthielten "15- und 20-Gallonen"-Holzöl-Phenolharzlacke 0,91 bzw. 1,04% Lösungsmittel nach Entfernung des gesamten Lösungsmittels sowohl durch Evakuierung als auch Desorption. Diese Werte liegen wesentlich niedriger, als die von Nitrozellulose- und Vinylharzlacken zurückgehaltenen Mengen. Der am langsamsten trocknende der geprüften Lacke, ein 40-Gallonen Rizinenolack, hielt 0,56% Lösungsmittel zurück.

Die Menge genügte doch schon, um die Wasserabsorptionswerte, welche man erhält, wenn exakte Messungen an Lacken, die nicht viel Wasser absorbieren, vorgenommen werden, drastisch zu ändern. Diese Wirkung wird ausführlich in einem zweiten Artikel, der sich mit wetterbeständigen Klarlacken für Aussen befasst, besprochen werden.

Сохранение растворителя в фенольных лаковых пленках

Резюме

При воздушной сушке покрытий небольшие количества растворителя сохраняются в пленке, так как сушка происходит наиболее быстро на поверхности. Поэтому покрытия которые высыхают наиболее быстро, улавливают наибольшее количество растворителя и эвакуация, даже при высоком вакууме, не удаляет всего сохраняемого растворителя. Удаление осуществляется только после ряда циклов поглощения и десорбции водой.

Количество растворителя улавливаемого в покрытиях модифицированных маслом по всей вероятности недостаточно чтобы повлиять на физические свойства покрытий. При расчете общего растворителя удаленного путем эвакуации и десорбции, на основании веса пленки высушенной воздухом, найдено что 15-ти и 20-ти галлоновые тунговые, масляные, фенольные лаки содержали 0.91 и 1.04 процентов растворителя соответственно, что намного ниже чем количества удерживаемые в нитроцеллюлозных и виниловых лаках. Наиболее медленно высыхаемый из испытанных лаков, 40-ка галлоновый дегидрированный кастор, сохранил 0.56 процентов растворителя.

Это количество, однако, достаточно чтобы существенно изменить значения водной абсорбции, полученных при проведении точных измерений на покрытиях которые не поглощают много воды. Этот эффект будет обсуждаться в подробности в добавочной статье посвященной прозрачным покрытиям для дерева в наружном применении.

Introduction

The rapid drying of lacquers occurs because of the fast evaporation of the solvents used in their formulation. To reduce lacquers to application viscosity, a solvent content of 70 to 80 per cent is required. Nevertheless, the lacquer coating is dry to the touch within a few minutes at room temperature, although a small amount of solvent is trapped within the film in the course of the fast drying. Even after the film has apparently dried, the retained solvent takes a very long time to evaporate completely, and this influences coating properties such as water absorption, hardness and other mechanical properties.

The Los Angeles Club¹ studied the effect of solvent release on hardness of lacquer films and observed that cellulose nitrate, although the fastest to harden, retained the most solvent. It was concluded that rapid hardening is due not

only to rapid solvent evaporation but also to other physical characteristics of the resin, in view of the greater solvent retention. Unplasticised vinyl lacquers, dried in air and under vacuum, retained 10 and 7 per cent solvent, respectively, whereas plasticised vinyl films retained less². Scherzinger³ evacuated lacquer films at elevated temperatures to remove solvents that would not leave the film under normal conditions and analysed them by gas chromatography. He also found measurable amounts of solvent in an acrylic film exposed outdoors for 2½ years. The evaporation of solvents from a dried film depends mainly on the rate of diffusion of solvents through the film. Residual solvents can be recovered by heating the film under vacuum⁴.

Murdock and Wirkus⁵ used radioactive tracer techniques and found that polymer films have a finite capacity to retain even very volatile solvents for a fairly long period. The capacity for solvent retention depends on factors such as the nature of the polymer, the type and concentration of modifiers and plasticisers, the volatility and type of solvents, the film thickness, and the mode of curing. Using carbon-14 tagged solvents, Hays⁶ could detect the presence of less than 0.01 per cent toluene in an acrylic film. He found considerable amounts of solvent retained in polymethacrylate films even under rigorous drying conditions. Several workers⁷⁻¹⁷ have studied the effect of high and low boiling point solvents on the rate of evaporation from lacquer coatings using different methods of measurement. Some have attempted to correlate solvent evaporation with drying, hardening, and application properties of such coatings.

Most of the methods and types of equipment for measuring the evaporation rate of solvents are used with freshly applied films. A thin-film evaporimeter fitted with dehumidifying and temperature control devices has been commonly used for such determinations^{11, 12, 18}. Highly sensitive techniques were recently employed to detect the presence of solvents in a coating after outdoor exposure for fairly long periods^{3-6, 19}.

The drying of oil-containing coatings differs from that of lacquers, and the release of residual solvents from them has not been studied in detail. When an oil-modified alkyd or a phenolic resin coating is dried under normal room conditions, the film first loses weight from evaporation of solvents. This is followed by a steady gain in weight owing to the absorption of atmospheric oxygen and concurrent polymerisation^{9, 10, 16, 20}. The more oil a coating contains the longer it takes to attain the stage of "touch dry." Hence, most of the solvents evaporate and only small amounts are trapped in the film. Short oil varnishes should be intermediate between lacquers and long-oil varnishes.

It is the purpose of this study to determine the retention and release of solvents trapped during air-drying of phenolic resin varnishes containing different types and amounts of drying oils. Because of the strong retention of trace amounts of solvents, it is not possible to use only high vacuum to measure solvent retention. It has been found in this laboratory that retained solvents are removed when the films are subjected to water absorption and desorption cycles. This paper reports the effect of oil on the retention of solvent by phenolic varnishes. Temperature and vapour pressure were controlled, unlike the water immersion tests commonly used in the paint industry.

Materials and procedure

Apparatus

The apparatus used for determining solvent retention in the dried free film is based on the McBain-Bakr sorption balance²¹. The film is suspended freely from a highly sensitive quartz spring (1mm extension \approx 0.4mg) in a long, wide, glass tube. The part of the tube holding the film is immersed in a thermostatic water bath controlled at $20 \pm 0.008^\circ\text{C}$. In one unit, four such tubes are fixed to a manifold connected to the vacuum line, a micromanometer, a vacustat and the water vapour source. The latter is immersed in another thermostatic bath so that the pressure of the vapour introduced in the system can be varied by raising or lowering the temperature of the second bath. Extension of the quartz spring is measured by cathetometer to 0.001cm and vapour pressure is determined by the micromanometer to 0.001in of mercury.

Materials

The phenolic varnishes used in the studies are listed in Table 1. Varnishes were prepared by heating the oil to 110°C to dissolve the resin and the mixture was heated to 240 to 260°C . Time of heating was controlled as much as possible to get a product of viscosity C—D (Gardner-Holt scale), when diluted to 50 per cent solids content.

Table 1
Composition of paraphenylphenolic varnishes

NRP No.	Oil content			Volatile content		Varnish properties	
	Type	Approx. length*	% on solids	Aromatic solvent	Mineral spirits	% solids	G-H viscosity
1,020	Tung	15	58.3	85.3	14.7	51	A-B
893	"	20	66.7	33.3	66.7	50	C
894	"	30	75	10	90	50	D
901	"	40	80	—	100	50	B-C
1,021	Linseed	15	58.3	49.4	50.6	49.5	D
902	"	20	66.7	30.6	69.4	51	B-C
903	"	30	75	20.2	79.8	49.5	D
905	"	40	80	10	90	50	C-D
1,022	Soya	20	66.7	28.6	71.4	50	B
1,023	"	40	80	34.7	65.3	50	C-D
1,024	Dehydrated	20	66.7	33.3	66.7	50	C
1,025	Castor	40	80	2.6	97.4	49	E

*Imp gal per 100lb resin

Shorter oil varnishes required more aromatic solvent to maintain clarity of dried films. Anti-skinning agent at a level of 0.3 per cent of the total weight was added to the cooled varnishes, which were stored in full containers in a cool room. As additional protection against skinning and to avoid viscosity increases, the cobalt and lead naphthenate driers were not added until shortly before the varnishes were to be used. The drier content as per cent by weight of oil content was 0.2 per cent lead and 0.02 per cent cobalt for the 15-gal tung oil

varnish, 0.3 per cent Pb and 0.03 per cent Co for the 20-gal tung, and 0.5 per cent Pb and 0.05 per cent Co for all others.

Procedure

Varnish films of uniform wet thickness were drawn down on 0.001in tin foil, using a blade of 2 mil clearance and a Gardner Laboratory film applicator. The films were air-dried in a dust-free room at $23 \pm 2^\circ\text{C}$ and 50 ± 2 per cent RH for three weeks. Free films obtained by amalgamation of the tin foil were dried under the same conditions for at least another three weeks before use. Films were cut into 1in squares and, after weighing, were mounted on a platinum loop and suspended freely from a quartz spring. The expanded length of the spring was measured and the system was evacuated below one micron pressure until the film attained constant weight. Most of the coating films reached almost constant weight after 48 hours under high vacuum. For subsequent work this was taken as the initial weight of the film.

Before admitting water vapour to the system, the water source was degassed intermittently. Repeated evacuation of the source removes traces of dissolved gases from water, so that only pure vapour is used in the tests. By controlling the temperature, water at a fixed vapour pressure is admitted to the system. In most cases, the water absorption equilibrium was reached within 24 hours, but the system was generally left for 48 to 72 hours before the final readings were taken. The corresponding gain or loss in the weight of the film from water absorption or desorption was measured with the cathetometer. To prevent condensation of water vapour on the film, tests were kept below 100 per cent RH. Desorption was followed by lowering the vapour pressure in the system by reducing the temperature of the vapour source in steps.

Analysis of retained solvents

The weight of the samples suspended from the quartz springs was not large enough to permit recovery of the retained solvents. In a separate experiment, pieces of free film (dry thickness 30 to 32μ) weighing approximately 4g were suspended on stainless steel hangers in a large desiccator. The desiccator was connected to the vacuum line via a cold trap. The system was pumped to below 1μ pressure for 72 hours, water vapour was then introduced in the desiccator at room temperature, and film pieces were left in water vapour atmosphere for 72 hours. The system was again evacuated; water vapour and traces of volatile products removed from of the film were collected in a specially designed cold trap. This cycle was repeated twice. The small, narrow tube in the bottom of the cold trap was dipped in liquid nitrogen and the upper part of the trap was warmed with a hot air blower so that any vapours it contained were condensed in the small tube, which was then sealed off. The tube contained water and a small quantity of organic matter. For analysis the tube was cut and covered with a rubber cap. About 0.05 to 0.1 ml carbon tetrachloride was injected and shaken gently to dissolve the organic material. The solution in carbon tetrachloride, being heavier than water, settled to the bottom of the tube and could be drawn out with a syringe whenever required for analysis. The organic matter recovered from the film in the course of water absorption-

desorption cycles was analysed by gas chromatography and infra-red spectroscopy.

Results

Loss in weight from evacuation

When the free films that had been dried for at least six weeks were first subjected to vacuum in the absorption apparatus, loosely-held solvents and oxidation products diffused out of them. As a consequence, the films lost weight, but constant weights were again attained after about 72 hours. Weight losses in percentages of air-dried film weight are shown in Table 2. It may be seen that the faster-drying tung oil varnishes lost more weight than did those made with other oils. Constant weight under vacuum was used as the basis for all subsequent weight changes.

Table 2
Initial weight loss on exposure to high vacuum
(Per cent by weight of air-dried film)

Type of oil	Per cent weight loss				Oil mean
	15gal	20gal	30gal	40gal	
Tung	0.602	0.621	0.541	0.462	0.557
Linseed	0.561	0.537	0.460	0.422	0.505
Soya	—	0.475	—	0.403	0.439
DHC	—	0.535	—	0.356	0.446

Loss in weight from water absorption-desorption

After removal of volatile material by high vacuum, there remains a certain amount of material held more strongly in the inter-molecular spaces of the film. This was gradually removed by repeatedly saturating the film near 99 per cent RH and then desorbing the water. The weight losses at the end of each absorption-desorption cycle are given in Table 3, and representative weight loss curves are shown in Fig. 1. Again, the fast-drying tung oil varnishes have a higher loss and take longer to reach equilibrium than do the slower drying varnishes. In Fig. 1, the dehydrated castor varnish maintained approximately the same weight during the last four cycles, the linseed varnish for the last three, and the tung varnish for the last two cycles. The 20-gal tung* lost slightly more weight than the 15-gal tung, probably because of the higher drier content, and lost considerably more than the 30- and 40-gal varnishes. With linseed varnishes in which drier concentration was uniform, the losses were inversely related to oil content. After six cycles, even the fastest-drying varnishes had practically ceased to lose weight. This means that water absorption values measured in the seventh cycle should not be affected by the presence of volatile ingredients.

*See Table 1 for the definition of this quantity.

Table 3
Weight loss of varnish films exposed to water absorption and desorption
 (Per cent by weight of evacuated film)

Absorp- desorp cycle	15-gal varnishes		20-gal varnishes				30-gal varnishes		40-gal varnishes				Cycle mean
	1,020 Tung	1,021 Linseed	893 Tung	902 Linseed	1,022 Soya	1,024 DHC	894 Tung	903 Linseed	901 Tung	905 Linseed	1,023 Soya	1,025 DHC	
1	0.092	0.093	0.102	0.070	0.062	0.057	0.061	0.072	0.065	0.068	0.059	0.075	0.074
2	0.182	0.175	0.210	0.121	0.130	0.106	0.126	0.116	0.121	0.146	0.106	0.092	0.136
3	0.274	0.226	0.289	0.180	0.192	0.175	0.182	0.178	0.169	0.182	0.164	0.147	0.197
4	0.351	0.286	0.367	0.235	0.209	0.217	0.249	0.232	0.228	0.197	0.207	0.195	0.248
5	0.398	0.319	0.430	0.276	0.212	0.222	0.290	0.257	0.249	0.234	0.215	0.197	0.274
6	0.411	0.323	0.448	0.285	0.215	0.222	0.305	0.259	0.247	0.236	0.211	0.204	0.284
7	0.418	0.319	0.455	0.285	0.218	0.222	0.307	0.259	0.251	0.240	0.215	0.208	0.288

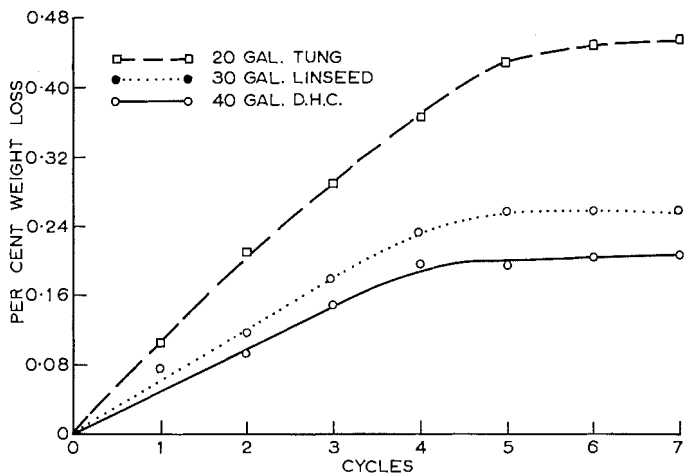


Fig. 1. Loss in weight with water absorption-desorption

Effect of drier content and drying conditions

The quick surface-drying properties of the 20-gal tung varnish seemed to be related to the high weight loss caused by both evacuation and water absorption-desorption. Experiments were therefore carried out to determine whether slower drying might lead to lower weight losses. This was accomplished by reducing the drier content and also by drying in the absence of oxygen.

The drier content in the 20-gal tung oil varnishes was 0.3 per cent Pb and 0.03 per cent Co. The same batch of varnish was used to prepare samples that contained 0.004 and 0 per cent cobalt respectively with 0.3 per cent Pb, and one with no drier at all. The effects of the changes in drier content are shown in Table 4. Films that are slower drying because driers are low or absent exhibit smaller weight losses. Reduction in cobalt, which is generally considered to be a surface drier, has a large effect on the weight loss of the dried and evacuated film. Elimination of lead, which is a "through" drier, has no effect.

Table 4
Per cent weight loss vs drier content

Absorp-desorp cycle	Drier content (per cent metal on oil content)			
	0.03 % Co 0.3 % Pb	0.004 % Co 0.3 % Pb	0 Co 0.3 % Pb	0 Co 0 Pb
1	0.102	0.072	0.063	0.081
2	0.210	0.181	0.142	0.148
3	0.289	0.248	0.215	0.201
4	0.368	0.289	0.263	0.282
5	0.430	0.351	0.304	0.341
6	0.448	0.395	0.365	0.348
7	0.455	0.400	0.365	0.352

Films of 20-gal tung varnishes containing 0.3 per cent Pb, and 0.03, 0.004 and 0 per cent Co respectively, were placed in a vacuum after a short exposure to air to allow the drying reaction to start, but solvent was removed by vacuum before the film had set. After 18 hours under vacuum (0 to 2 in Hg), the films were allowed to dry normally before free films were prepared. The varnishes containing cobalt were, in fact, dry at the end of the vacuum period. The weight losses obtained by subjecting the films to water absorption-desorption are given in Table 5. It may be seen that drying in a vacuum had a much greater

Table 5
Per cent weight loss of films evacuated for 18 hours before normal drying

% Cobalt	0.03 %	0.004 %		0
% Lead	0.3 %	0.3 %		0.3 %
Minutes before vacuum	30	30	5	30
Cycle No.				
1	0.091	0.063	0.048	0.059
2	0.143	0.157	0.109	0.094
3	0.223	0.157	0.117	0.124
4	0.263	0.176	0.109	0.171
5	0.293	0.251	0.137	0.190
6	0.308	0.251	0.158	0.204
7	0.315	0.240	0.158	0.209

effect in reducing weight loss than did lowering the drier content. For example, a film containing 0.004 per cent Co that was exposed to air for only five minutes, lost less weight than one with no cobalt that was left in air for 30 minutes.

Identification of recovered products

The carbon tetrachloride solution of the volatile material obtained from larger pieces of varnish film was subjected to gas-liquid chromatography using two different columns. In one series of tests, the stationary phase was Carbowax 1,540 on 110 to 120 mesh Anakrom AS. The 9ft column was maintained at 100°C with an inlet temperature of 160°C. In other tests, a 150ft capillary column treated with Ucon 550-LBX was used with a programmed temperature rise of 2°C per minute. Comparisons were made with chromatograms obtained under the same conditions from a 4 per cent solution of mineral spirits in CCl_4 . More information was deduced from the capillary column results. The sample exhibited peaks corresponding to those for decane, undecane, dodecane and tridecane, which are found in mineral spirits. Many very small peaks not detected in the reference solvent chromatograms were present in those from the sample.

The sample solution was also cast on a sodium chloride plate and its infra-red spectrum obtained with a grating-equipped spectrophotometer. The largest absorptions occurred at wavelengths assigned to CH_2 and CH_3 groups and alkane chains. Expansion of the absorption scale indicated small amounts of carbonyl compounds. It was concluded that the recovered material was chiefly composed of hydrocarbons similar to those in mineral spirits, with trace quantities of ketones from the oxidation products of the film.

Discussion

The results show that solvents are trapped in air-dried varnish films, especially those that surface dry rapidly. This entrapment occurs because, after application, the surface becomes viscous and then immobile, owing to solvent evaporation and oxidative polymerisation. Meanwhile, because it takes time for solvent to diffuse out and oxygen to diffuse in, the coating in contact with the substrate is still liquid and contains solvent. Once the surface becomes dry to touch, solvent release follows the laws of diffusion through solids^{22, 23, 24}. Such diffusion is directly proportional to the vapour pressure difference across the film and inversely proportional to the thickness. Solvent retained in a coating applied to an impermeable substrate will, therefore, diffuse through the film until equilibrium is reached between its vapour pressure within the film and that in the local environment.

Because there is, for practical purposes, no solvent present in the atmosphere once the bulk of the solvent has evaporated, diffusion should continue until no solvent is left in the film. Escape of the last few per cent of the solvent is, however, very slow because resistance to diffusion increases as the film solidifies and because the vapour pressure difference across the film is low. Forces of attraction, such as hydrogen bonding between the solvent and film components, may be strong enough to counteract the vapour pressure differential. For these reasons, solvents may be detected in coatings even after outdoor exposure for more than two years³⁻⁶.

Evacuation of the air-dried film speeds up attainment of the equilibrium that would ultimately be reached in air by removing air molecules, which slow down solvent evaporation. When free films are used, both sides are available for diffusion and this assists in rapid attainment of equilibrium. Part of the observed weight loss is due to removal of water absorbed when the film was maintained at 50 per cent RH. In normal curing, slow-drying coatings do not reach the touch-dry and hard-dry stages for several hours, and this longer drying period allows more time for solvent to evaporate from the film. Hence, the loss in weight due to evacuation is less for phenolic varnishes prepared with soya, dehydrated castor, and linseed oils than it is for the rapid-drying tung-oil varnishes. In varnishes made with the same oil there is more solvent trapped in the short-oil varnishes, where solvent evaporation plays an important part in the drying process, than in the long-oil varnishes.

When the evacuated film is subjected to almost 100 per cent RH, water diffuses into the film until it is saturated at equilibrium. There is probably some swelling because the water interferes with hydrogen bonding between polar components of the film. Water molecules would also displace hydrogen-bonded solvent because water is more polar than most organic solvents²⁵. In addition,

retained solvent would dissolve in the absorbed water in proportion to its distribution coefficient between water and the dry film. When the external water vapour pressure is lowered and desorption takes place, the swollen condition of the film and the displacement of trapped solvent allows more of the solvent to escape than is the case with simple evacuation. The release of some of the solvent provides added space for water to be absorbed during the next absorption cycle. The additional water causes more swelling and more solvent is lost on the second desorption. This continues in subsequent cycles until all solvent is removed and the true dry weight and water absorption values of the film are obtained. The same relation between fast-drying and solvent retention was obtained with water absorption-desorption as with the evacuation tests.

The results of weight losses from absorption-desorption of films of short-oil tung varnishes, the drying of which was retarded because driers were reduced or absent or because air was removed during the first drying period, also indicate that rapid drying causes solvent entrapment. Reduction or total absence of cobalt drier, which promotes surface drying, slows down the drying rate. This results in the retention of less solvent in the dry film, as shown by the lower weight loss after the same number of cycles. When films are placed under vacuum shortly after application, there is a marked reduction in subsequent weight losses. This is attributed to the decrease in rate of oxidative polymerisation and also to the faster evaporation of solvents in a vacuum. Film evacuated within five minutes of preparation consequently showed the lowest retention of solvents of all the varnishes tested.

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