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SHELLAC DRYING OIL COMBINATIONS,

PART I.

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In the past the price of shellac has varied between wide limits, and at times has been very high. This all important factor has undoubtedly discouraged enquiry into the possibility of extending the uses of this resin. This is not the place to discuss the future price of shellac, yet it may be said that the powerful economic factors, such as the effect of synthetic substitutes and the effect of better and surer means of cultivation, which have begun to operate in recent years, must surely have a big stabilising influence. It would appear quite possible therefore, that shellac may continue to be a cheap resin. This opens up many new fields of possible use. Of these, one that has been but superficially examined, is that of shellac drying oil combinations.

Apart from price, the great obstacle to the use of shellac in this connection was the incompatibility of shellac with drying oils under the usual condition of varnish manufacture. The only method of incorporating shellac with drying oils which was generally known and used depended on the effect of a relatively large proportion of lead in inducing shellac to dissolve in hot linseed oil. It is difficult to ascertain when this discovery was made ; undoubtedly it was preserved as a trade secret for many years. One of the earliest references to this use of shellac was made by Charles F. Crockett (1) in 1867. Since then the process has been patented (2) and many text books of varnish technology have included a formula, *e.g.*—

Shellac Gold size [Bearn (3)]

T. N. shellac	100 lbs.
Prepared oil	30 gals.
Red Lead	40 gals.
Turpentine	100 gals.

Pale Grinding Japan [Sabin (4)]

Shellac	4 lbs.
Oil	2 gals.
Litharge	4 lbs.

Temperature not to exceed 340°F.
Manganese liquid drier added ...

Shellac Grinding Japan 1, [Scott (5)]

Linseed oil	50 gals.
Red lead	80 lbs.
Manganese dioxide ...	20 lbs.
T. N. shellac	48 lbs.
Litharge	20 lbs.
Wood Turpentine	64 gals.
Heavy Naptha (48°F) ...	56 gals.

Shellac Grinding Japan 2, [Scott (5)]

Linseed oil	50 gals.
Red lead	64 lbs.
Manganese dioxide ...	16 lbs.
T. N. shellac	32 lbs.
Resin	32 lbs.
Litharge	32 lbs.
Wood turpentine	60 gals.
Naptha (54°F)	50 gals.

In all these formulæ the amount of lead is relatively very large. The possibility of incorporating shellac with drying oils with less lead, or by other means entirely, has been investigated.

A number of ways of inducing shellac to disolve in drying oils have been elaborated, and have been described in this preliminary paper. It is hoped later to examine the properties of these shellac—drying oil combinations and the possibilities of their use in preparation of varnishes, paints, adhesives, cements, etc.

Experimental.

If shellac and linseed oil are heated together the shellac first melts and after a certain time, depending on the temperature, 'cures' and separates as a spongy mass. It is commonly considered (7), therefore, that shellac is insoluble in hot linseed oil. It can be demonstrated, however, that the 'curing' and separation of shellac can be avoided if certain precautions are taken.

Condition necessary for direct solution of shellac in hot linseed oil.—The oil must be heated to 380°—390°C and the shellac, reduced to a powder, added slowly. The temperature of the oil must be maintained at 380° during this addition. When the shellac has been added the solution should be cooled quickly to prevent the whole "jelling". This process can be easily carried out on a small laboratory scale. On a large commercial scale practical difficulties will undoubtedly arise. A continuous process, dealing rapidly with small quantities, should be succesful however.

Lower temperatures may be used if the shellac and oil are heated under pressure. Samples of shellac and linseed oil heated in sealed tubes at 320°C gave satisfactory solutions.

In order to incorporate shellac with oil at lower temperatures in open vessels various other means have been investigated.

Lead as an incorporating agent.—The process of dissolving shellac in oil by use of lead, which is the method used in actual practice, was examined.

A large number of experiments were conducted with varying proportions of litharge, shellac and linseed oil. Comparison of formulæ which resulted in solution with those which produced 'curing' demonstrated that the important factors to ensure solution were (*a*) the ratio of lead to linseed oil, (*b*) the temperature of introduction of the shellac (*c*) the amount of shellac.

Consider the following formula :—

28	parts by weight of	shellac
36	,, ,, ,,	,, linseed oil.
1	,, ,, ,,	,, litharge.

The litharge is incorporated with the linseed oil by heating at 220°C until reaction is complete. The temperature is then raised to 290°C—300°C and the powdered shellac added slowly, maintaining the temperature at 290°C (approx). Heating is continued until a drop, cooled on a glass plate remains unclouded. The oil shellac solution is then cooled to avoid "jelling". If the shellac is added at a *lower* temperature that 290°C it 'cures' and separates. If more than 28 parts of shellac are added the excess 'cures'.

By increasing the amount of litharge the temperature of addition of shellac may be lowered as recorded in the following table :—

Ratio of litharge to oil.	**Min. temp. of addition of shellac.**
1 : 6	220°C ... ...
1 : 10	250°C ... ...
1 : 18	270°C ... ...
1 : 36	290°C ... ...

Increasing the amount of litharge does not appreciably affect the amount of shellac which may be added without 'curing'.

Other materials as incorporating agents.—Experiments have been conducted on the possibility of incorporating shellac by means of materials other than litharge. A number of such materials have been found. It has been established that conditions similar to those pertaining to use of litharge are important for successful incorporation, *e.g.* (*a*) the ratio of incorporating agent to oil (*b*) temperature of addition of shellac (*c*) amount of shellac.

It has been established that certain other metalic salts behave in a similar way to lead, *e.g.* oxides and carbonates of sodium, potassium, calcium, barium and magnesium. A typical formula consists of—

20	parts by weight	shellac
40	,, ,, ,,	linseed oil.
1	,, ,, ,,	calcium oxide.

The lime is added at 250°C, and when the oil has cleared the temperature is raised to 290°—300°C and the shellac added. With a larger proportion of lime lower incorporating temperatures can be used.

Most other metalic salts including oxides of manganese and cobalt do not assist the solution of shellac in oil.

Glycerine is a useful incorporating agent. The following is a typical formula :—

4	parts by weight	glycerine.
10	,, ,,	linseed oil.
6	,, ,,	shellac.

The glycerine and oil are heated to 270°C and the shellac added slowly. A small addition of litharge, sodium carbonate, etc. enabled less glycerine to give a satisfactory solution.

Rosin was found to be a very successful incorporating agent. The following is a typical formula :—

9	parts by weight	rosin.
10	,,	,,	linseed oil.
9	,,	,,	shellac.

The shellac is added at 250—270°C.

Materials similar to rosin which were successful included **ester gum, albertol IIIL** (presumably due to its rosin content) **stearic acid,** etc. A typical formula consists of :—

12	parts by weight	albertol IIIL.
10	,,	,,	linseed oil.
9	,,	,,	shellac.

The shellac is added at 250—270°C.

Certain **high boiling solvents,** *e.g.*, tricresyl phosphate (b. p. 300°C), triphenyl phosphate (b. p. 245), triacetin (b. p. 259°C) etc. can be used as incorporating agents. A mixture of about 10 parts of linseed oil, 8 parts of solvent and 8 parts of shellac is heated until the solvent has evaporated and the shellac remains in solution in the linseed oil.

Solvents with somewhat lower boiling points, *e.g.*, benzyl alcohol (b. p. 205), aniline (b. p. 185) etc. do not assist solution of the shellac. When the solvent has evaporated off from the oil the shellac separates and 'cures'.

A modified shellac which is oil soluble may be prepared from rosin with glycerine, lime, magnesia, etc. as hardening agents, *e.g.*—

20	parts by weight	rosin.
16	,,	,,	shellac.
1	,,	,,	calcium oxide.

are heated together to 280°C. This resin dissolves in oil previously heated to 250°—270°C. Similarly a mixture of rosin and shellac may be esterified with glycerine and the resulting ester dissolves in oil heated to 270°C.

If at any stage in the preparation of the shellac oil solution the shellac separates and 'cures' due to incorrect conditions, the whole should be immediately cooled and the 'cured' shellac separated off. This material may be 'reconditioned' by the following process : The 'cured' shellac is powdered and slowly added to rosin heated to 270°C. Five parts of rosin will dissolve about three parts of this shellac. A small proportion of glycerine may be added. The resulting 'ester' will dissolve in linseed oil heated to 270°C. Shellac which has been rendered infusible by other means such as 'overcooking' in solvent recovery, bad storage of both ordinary and bleached shellac, etc. can be 'reconditioned' by the above process and dissolved in oil.

In certain cases it has been observed that shellac which has 'cured' owing to incorrect proportions of incorporating agent may be dissolved if the temperature is rapidly raised. This is not recommended as a useful method, however, owing to its uncertainty.

The possibility of incorporating shellac in tung oil.—It is apparently impossible to persuade shellac and tung oil alone to give a solution. At 290°C the tung oil "jells" and this temperature is too low for incorporating shellac. Even under pressure it appears impossible to effect solution without causing the whole to "jell".

Most of the methods described above, however, in which incorporating agents are used can be utilised to induce shellac to dissolve in tung oil. Sufficient of the incorporating agent must be present to allow of addition of shellac at a temperature below 270°c otherwise the oil may "jell", *e.g.*, using lead, the ratio of litharge to tung oil should be about 1 : 10.

Preparation of "Long-Oil" varnishes.—Most of the above methods of incorporating shellac produce relatively "short-oil" solutions. Long oil varnishes can be prepared from them if certain precautions are taken. The oil to be used as diluent should be "blown" or thickened, heated to about 270°C, and slowly added to the shellac varnish also heated to 270°C. The varnish, which becomes cloudy on addition of the oil, becomes clear on continued heating. Tung oil varnishes may be heated until they "string". Linseed "short-oil" varnishes may be conveniently diluted with tung oil.

Most of the above varnishes may be diluted with up to two volumes of oil per volume of original varnish.

Volatile diluents.—The above varnishes are all soluble in the usual varnish diluents, *e.g.* turpentine, toluene, benzine, white spirit + solvent naptha, etc. A mixture of turpentine with 25% toluene appears to be an excellent diluent.

Type of shellac.—In all the above experiments a sample of fresh "ari" Kusum shellac has been used. Most shellacs are also suitable, but certain indications have been obtained that fairly old shellac may need larger proportions of incorporating agents to give a solution.

Discussion.

Shellac when heated alone very readily "cures" to a spongy insoluble product. The rate of curing depends on the temperature: at 240°C "curing" takes place in a few seconds. It has been established (8) that the rate of "curing" can be considerably retarded by certain conditions. These include pressure, presence of solvents, glycerine, rosin, alkaline oxides and carbonates. These facts together with an assumption that shellac tends to become soluble in drying oils at high temperature offer an explanation of the various precautions described above. The process is a race between solution and "curing". At 380°C shellac is sufficiently soluble in linseed oil to be able to go into solution before it "cures". At lower temperatures, *e.g.* 320°C shellac is sufficiently soluble to go into solution provided "curing" is retarded by pressure. At still lower temperatures powerful retarders such as excess of rosin, glycerine, and other high boiling solvents must be present to give the shellac time to remain in contact with the oil and eventually dissolve.

In the incorporating process using lead, sodium and calcium salts, it is possible that the shellac tends to dissolve in the soaps formed. These together with the glycerine formed by saponification should sufficiently retard the curing of the shellac.

The above methods of incorporating shellac have been described as "solution". It is possible, however, that a reaction really occurs between the shellac and the hot oil. The large amount of foam formed, which is always a sign that the shellac is being satisfactorily incorporated, is evidence in favour of this. In any case, it is certain that the shellac itself undergoes considerable change. A study of the properties of these shellac oil "solutions" should give interesting results.

It may be well to emphasise that the formulae and methods described are only intended to illustrate the general principles of the process of incorporating shellac in drying oils. Many of the methods may be of no practical value; others will have to be considerably modified by the practical varnish maker to ensure correct "cooking" of the oil, incorporation of correct proportions of drier, etc.

Summary.

Conditions of temperature and pressure necessary to dissolve shellac in linseed oil are described. The temperatures are somewhat high, however. In order to incorporate shellac in linseed oil and tung oil at lower temperatures, *e.g.*, in the region 230°—280°C other methods have been described using certain incorporating agents. These latter include rosin, glycerine, albertols, ester gum, and certain salts of lead, sodium, potasium, barium, calcium and magnesium.

It has been demonstrated that important factors for satisfactory solutions are (*a*) ratio of incorporating agent to oil (*b*) temperature of addition of shellac.

The short-oil solutions prepared by these means may be diluted with hot oil to give long-oil varnish under certain conditions. Thus the final ratio of incorporating agent to oil may be made quite small.

Methods are described for preparing oil soluble resins from shellac which has 'cured' owing to overheating, long storage, etc.

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