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ORPIMENT IN SHELLAC

BY

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Since the earliest days of shellac manufacture orpiment, the naturally occurring yellow sulphide of arsenic, has been incorporated in shellac to modify the colour to meet trade requirements. In recent years the need for reform in the marketing of shellac has been realised and the desirability of this inclusion of orpiment questioned. In 1930 the United States Shellac Importers Association gave active consideration to the question. The possibility of a universal standard of arsenic-free shellac or a fixed limit to the amount of orpiment content was debated. The Indian Shellac trade was communicated with concerning the 'proper maximum for arsenical content' at the same time 0.2% was suggested as the proper content in their opinion. This communication disclosed the conflicting views held in India on the subject. The need for a careful survey and examination of the properties of "Orpimented" shellacs was indicated and was undertaken in this laboratory. Some of this work has already been published; this together with certain experiment recently completed will be discussed in this paper.

The general scheme of the experimental work consisted of examining the various properties of shellacs containing orpiment and comparing them with control, orpiment-free samples, prepared from the same seedlacs. The samples, prepared in the experimental lac factory attached to the Institute, consisted of a large range containing varying amounts of orpiment made from representative qualities of seedlac. The various important properties will be discussed.

The Iodine value of shellac.

The effect of orpiment in raising the iodine value of shellac was mentioned by Parry (1) in 1903, and again by Briggs (2) in 1925 although Langmuir (3) in 1911 had stated that it had no effect. The correctness of Parry's view, which has for some years now been generally accepted by the Trade, was definitely established by Rangaswami and Aldis (4) who give figures for the magnitude of the effect.

In the past this effect has caused a certain amount of confusion. Shipments of pure fine orange shellac owing to high orpiment content have given an iodine value above the stipulated 18 of the American Shellac Importers Association and have been condemned as a consequence.

It has been pointed out by Aldis (5) that the Iodine value of pure shellac is probably nearer 16 than the standard 18 for rosin free shellac. This margin of 2 is necessary, however, owing to the effect of small quantities of orpiment which may be present. The abolition of orpiment would enable the standard to be lowered by at least one unit and should do much to encourage the production of purer shellacs.

Orpiment and the Bleaching of Shellac.

The effect of orpiment on the shellac bleaching process has been examined in this laboratory. It has been definitely established that shellacs containing orpiment require more bleach than their controls. This extra amount is small if the shellac contains less than 0.3% orpiment. In all cases orpiment imparts a slight colour to the bleached shellac. To obtain pure white, best quality bleached shellac only orpiment-free material should be used. This result is in agreement with the universal opinion solicited from American and European bleachers.

The importance of this effect of orpiment has been considerably diminished in the last year owing to the almost universal preference for seedlac instead of shellac for bleaching. Certainly if shellac ever returns to popularity for bleaching an orpiment-free shellac will be demanded.

Orpiment and the colour of shellac varnishes.

Opinions on the effect of orpiment on the colour of the spirit varnish prepared from shellac have in the past been conflicting. Fowler (6) states that "The object of adding orpiment is not merely to colour the lac yellow, but to remove, by a pyrochemical reaction with the orpiment, a certain amount of residual red or purple colouring matter which may be present in the lac granules." This effect, if it occurs at all, must be extremely small, however. It has been demonstrated by Rangaswami (7) that the colour of filtered varnishes, prepared from orpimented samples and their controls, showed no difference of practical importance ; the orpiment is apparently filtered off unchanged.

Orpiment and the protective properties of shellac varnishes.

A comparison of the properties of varnish films prepared from orpimented shellacs and their controls have been made by Rangaswami (7). It is evident that the effect of orpiment on the 'scratch hardness', 'abrasion resistance', water resistance, and weathering properties is too small to be of any practical importance. Rangaswami claims that orpiment has an effect of lowering the abrasion resistance and scratch hardness but the amount of evidence given and the possible experimental errors of the method hardly justify this. It suffices, however, that orpiment can definitely be excluded from shellac without adversely affecting the protective properties of the resulting varnish.

The Fluidity of Shellac.

The 'fluidity' of molten shellac measured at a definite temperature is a very varying property. Heat treatment, action of acid fumes, long storage etc. affect big changes in this value. This loss of fluidity is an undesirable property for certain uses of shellac e. g. in manufacture of thermo-plastics, sealing wax, etc. The possibility of orpiment modifying this property has been examined.

The fluidity was measured at 125°C by the Metropolitan Vicker's apparatus taking the usual precautions (8). The samples examined included (a) samples stored for varying times and (b) samples subjected to a low temperature 'cure' at 38°-40°C for several days. In all experiments no appreciable difference could be detected in the fluidity of orpiment samples and their corresponding controls.

"Life under heat".

The "Life under heat" is a measure of the time taken for shellac to 'cure' to an infusible material at a fixed temperature. It is of special importance in the thermo-plastic industry. The property was measured by a modification of the Westinghouse method. The sample, contained in a flat bottomed glass tube, was heated in an oil bath to 150°c. The time taken to 'cure' and reach the 'rubbery' stage, as indicated by the twisting back of a glass rod immersed in the shellac, was recorded. In all experiments no difference in the 'life under heat' was observed between orpiment samples and their controls.

Orpiment and the Elasticity of Shellac.

The opinion is held by some that orpiment reacts with shellac in some way and affects its mechanical properties. Livache and McIntosh (9) state that orpiment probably exerts a vulcanising effect and to this 'in a great measure is due the nerve and spring and elasticity of orange shellac'. Fowler (6) shares this opinion and states that 'a sort of vulcanising effect appears to be produced in the resin. Orpiment appears to be specific in its action and cannot be replaced by other sulphides'. These views have not been substantiated by experiments conducted in this laboratory. Samples were tested for 'breaking strength' i. e. the force required to bend and break a standard test piece. Accurate dererminations were not possible owing to difficulty in selecting uniform test pieces from the shellac ; the experiments were sufficiently accurate, however, to demonstrate that orpiment had no appreciable effect on this property. Moisture content, wax content, heat treatment and age are the factors which influence this property to an appreciable extent ; the temperature and humidity of the atmosphere at time of determination having also a big influence.

It is apparent, therefore, that examination of the properties of orpimented shellacs have produced no evidence that orpiment serves any useful purpose whatsoever. A brief survey will now be made of other opinions on the subject.

Opinions of certain members of the Trade.

Opinions have from time to time been obtained from members of the consuming industries. These opinions are unanimous in agreeing that inclusion of orpiment is useless. In most industries the orpiment is looked upon as a harmless adulterant. Certain industries, however, claim that this material has undesirable effects ; e. g. the following is quoted from a journal of the Hatting industry (10) which consumes about 10% of the world's production of shellac :—"To render perfect alkaline solution, these lacs must be free from two adulterants rosin and arsenic sulphide (orpiment)..... Even to-day we hear of the possible necessity of these two adulterants in the lac composition.....the second, the arsenic salt, has a more pernicious effect on the proof, rendering it harsh and unable to enter the fibre..... The white lac must be absolutely free from (a) colophony (b) chlorine, free or bound (c) arsenic and lead salts etc."

The opinion of the shellac bleaching industry has already been indicated. Orpiment is very definitely undesirable.

A firm of shellac manufactures, who engage a small research staff and whose opinion should therefore carry some weight, have for many years opposed the use of orpiment. Their answer to the American enquiry as to the proper amount of arsenic in shellac was brief and to the point—"None".

Gibson (11) in his annual report has very definitely condemned orpiment from every point of view. His opinion may be taken as a consensus of the views of most of the consumers of shellac, many representatives of which have been personally interviewed.

Other arguments against the use of orpiment.

The price of orpiment, compared to the present price of shellac, is somewhat high. It costs about Rs. 50 per maund and the process of incorporation is very wasteful. This has encouraged enquiry into the possibility of using substitutes. A material was placed on the market in Calcutta described as "Orpiment ground and prepared ready for incorporation". This contained about 40% arsenic sulphide and 40% lead chromate admixed with silica etc. Fortunately the Indian Shellac Manufacturer has developed a certain amount of respect for the likes and dislikes of consumers and this material was treated with suspicion and was never popular. A certain amount of shellac using this adulterant was put on the market, however. The undesirability of incorporating such hitherto unsuspected material as lead in shellac is obvious e. g. the possibility of the presence of lead in any batch of shellac would condemn it for use in the munition industry.

Shellac varnish is sometimes used in edible materials such as chocolates etc. and on food containers. Unnecessarily high prices have been paid for shellac for these uses to ensure that it is orpiment free. This has encouraged the use of other varnishes in this field.

The possible effect of orpiment on workers in shellac factories would appear to be an argument against its use. S. Mahdi Hassan (12) describes the use of orpiment as 'extremely dangerous for those who have to use it, whilst fumes emited during the fusion process are poisonous'. O'Connor (13) in one of the earliest records of shellac manufacture quotes an opinion : "Dr. Chevers says that the use of arsenic sulphide gives rise to miliary eruptions on the bodies of the workmen". In a personal tour of many shellac factories in Mirzapur, Balrampur, Jhalda, Ranchi etc. it appeared that actually very little harm comes from working

with orpiment. No information of cases of arsenic poisoning or any effect of orpiment on the work-people could be elicited. It is possible that those using this material have developed resistance to it or learned to take necessary precautions. It is also possible, however, that many illnesses, due to arsenic poisoning, are never diagnosed as such. It is no uncommon sight in a lac factory to see a small baby playing with orpiment with its hands and face yellow with the pigment. Infant mortality is so common, however, that this danger is presumably one of the lesser ills a child has to contend with in India. Concerning the fumes arising from orpiment it may be stated that harmful effects may result if this material should be inadvertently thrown on to the charcoal fire in the badly ventilated melting rooms.

The present low price of shellac and the possibility of it continuing to be low priced has begun to encourage enquiry into new uses for this material. It is, of course, impossible to fortell what these uses may be; but it would be unfortunate if certain fruitful enquiries should be discouraged owing to uncertainty of impurities such as orpiment. A case which occurs to the mind is the use of a modified shellac as a constituent of chewing gum where orpiment would be definitely detrimental.

Concerning the American proposal that the amount of orpiment permissible in shellac should be limited, it may be pointed out that this would be a very undesirable arrangement. The process used for incorporating this material is such that it is extremely difficult to ensure getting a definite amount into the shellac. Such variable factors as the size of the mesh of the bag, the state of division of the orpiment, the nature of the impurities in the seedlac etc. exert a big influence. Many cases would arise where the unfortunate manufacturer would unknowingly exceed the 0.2% limit and would be penalised. Except for the advantage the consumers would get from 'allowances' there appears to be no point in making this standard.

The original purpose for which orpiment was included in shellac may be brought to question. The object was to enable the manufacturer with a blend of seedlacs of varying colour and quality to keep up a fixed standard of colour in his shellac. The consumer has now learnt, after years of sometimes costly experience, that the colour of shellac is a very uncertain criterion of the useful properties of this material. The need for other standards for shellac such as 'bleachability', insolubility, fluidity etc. has been realised and every effort should be made to establish them. If shellac is to hold its own against

the competition of synthetic substitutes, adopting modern methods of salesmanship, it must adopt these modern methods itself. It must certainly go off the 'colour standard', when a bad colour can be so readily disguised with a useless material such as orpiment.

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