TABLE IV

Epoxy Esters Based on Tall Oil Acids

	Composition				Constants		Air dry properties 0.04% Co 3 mil wet					
									Sward hardness			
Epoxy type	Epoxy wt	DCOFA wt	TOFA wt	IPA	Viscosity	Solids solvent	Tack free	Foil dry	3 days	28 days	Denude 70C 1% Tide ®	Times R.T. 3% NaOH
A) Terpene-epoxy.....	66.7	16.6	16.7	....	S	50% Xylol	1:00	2:30	50	70	2100	1900
B) Terpene-epoxy.....	65.3	...	32.6	2.1	V	50% Xylol	:45	3:00	30	72	550	1680
Bisphenol	60	40	...	.	U	50% Xylol	:55	2:30	22	64	550	890

DCOFA = dehydrated castor fatty acids (Baker 9–11 type).
TOFA = low rosin tall oil fatty acids (Acodar—Newport Industries).
IPA = isophthalic acid

Epoxy Esters. In order to provide highly resistant coatings systems necessary to meet the demands of premium applications, an epoxy resin "backbone" is frequently the answer. By incorporating tall oil acids into the formulation of esters, significant cost reduction can be achieved. Our laboratory has prepared a terpene-phenol glycidyl ether derivative (5) which in its esters has shown unusual chemical resistance, solvent miscibility and resin compatibilities as compared with the common bisphenol types.

Tall oil acids have been used in two ways in this segment of work: a) as partial replacement of the more costly dehydrated castor fatty acids, and b) as the sole fatty acid component. Table IV describes the formulations, resins and properties obtained.

The procedure used in the case of the split fatty acid cook was as follows: To a similar system used in the preparation of the alkyd resins were charged 66.7 parts of "T" resin (5), 16.6 parts of dehydrated castor fatty acids, four parts of xylol to maintain reflux as the azeotrope-former. The mixture was heated to 260C in two hr and held until the acid number reached 10. The remainder of fatty acid (16.7 parts of tall oil acids) was then added and the reaction continued at 260C to an acid number less than 10. The resin was cooled to 140C and then diluted with the appropriate solvent.

It appears from the data presented in Table IV that tall oil acid based epoxy esters may be made with high performance features. Resin B described in the above table has the unique balance of properties for use as a dip coating vehicle requiring stability of the resin at application temp of 125F with rapid conversion at 400F baking temp. A vehicle of these qualities may find use in washing machine primers and topcoats, electrical equipment finishes, etc.

Conclusions

Tall oil fatty acids have been used in the preparation of new types of alkyd, urethane alkyds and epoxy esters. Fast drying durable resins are provided for use in trade sales, metal decoration, primer and topcoat applications.

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Mechanically Aided Thin-Film Evaporation as a Tool for the Tall Oil Industry

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Abstract

This article describes the thin-film evaporation process and emphasizes its values in applications where heat sensitivity, high viscosity and low thermal conductivity are important processing factors.

Processing Tall Oil

MANY PRODUCTS in the tall oil industry can be processed efficiently by thin-film evaporators since there are literally hundreds of tall oil products which are viscous, or heat sensitive, or both.

But tall oil products vary a great deal in composition. Thus, it becomes difficult to generalize on the applicability of the thin-film evaporator to these products A number of tests which have been performed illustrate, however, the applicability of thin-film evaporation in tall oil processing.

One series of tests showed that valuable materials such as tall oil fatty acids could be recovered from waste tall oil pitch by thin-film evaporation. Since the residue becomes very viscous as products are separated, distillate rates are low in this operation, averaging 5–10 lb/hr/sq ft.

Tests have also been run on tall oil products whose yield rates and maximum Gardner colors were specified. Distillation rates here varied from 15–35 lb/hr/sq ft due mainly to the less viscous nature of the material. Similarly, work has been done on a tall oil fatty acid where the object was to remove color bodies to improve Gardner color from a No. 7 to a No. 3 or No. 4. Distillation rates ranged up to 38 lb/hr/sq ft.

An excellent application is the separation of monomer from dimers and trimers in a dimerized tall oil fatty acid. Distillation rates ran up to 50 lb/hr/sq ft.

The other component in crude tall oil—rosin—has also been tested and distilled by thin film units with good results. Distillation rates average 20–22 lb/hr/sq ft. Operating pressure in these tests varied from 1–5 mm Hg absolute.

Such test results are hardly conclusive, but they are indicative of potential benefits to be derived from thin-film processing in the tall oil industry.

Thin-Film Evaporators

Let us take a closer view of this processing method to find out how and why it works. Thin-film evaporation theory is based on the fact that if you evaporate products that are heat sensitive or viscous you need 1) a large surface to vaporize and separate effectively, and 2) a thin layer to provide quick and efficient heat transfer. The problem has been how to provide both in a practical design.

Modern thin-film evaporators have overcome many of their initial shortcomings, most of which related to fabrication limitations. Today, mechanical methods, based on centrifugal force generated by a rotor, distribute the product as a thin-film over the entire heat transfer surface. The thin-film increases heat transfer efficiency and makes it possible to take advantage of the benefits derived from low retention time in an evaporation system. One-pass operation is possible in most cases. Consequently average holding time is reduced. Higher temp can be used without danger of thermal degradation because time-temp relationships are kept in balance.

Actually, the principle of operation for mechanically-aided thin-film evaporators is simple. A small amt of liquid is continuously fed into the top of a still, usually from a number of openings. The liquid flows down the evaporator wall by gravity, and, aided by mechanical wipers, forms a thin-film that covers the evaporating surface. Thus only a thin-film of liquid is heated at any given time.

Relative to cost, mechanically aided thin-film units are more expensive than conventional evaporators on a price/sq ft basis, but the cost is by no means prohibitive. The units become much more economical as the size increases. A 4-sq ft unit costs approx $2,000/sq ft, but a 100 sq ft unit costs only ca. $300/sq ft. It should be remembered that the price differential between standard evaporating equipment and thin-film units is not so significant when total installation costs are taken into consideration. Instruments, pumps, tankage, and other auxiliary equipment, plus the installation itself, represent a greater portion of the total cost of a system than the evaporator alone; and auxiliary equipment is apt to be the same with either installation.

Nevertheless, if an evaporation process can be accomplished satisfactorily in a calandria, natural or forced circulation evaporator, etc., thin-film units should not be considered unless superior qualities of the product are needed. An economic study in such a case should take into account the higher yields and superior color obtainable in thin-film units. Superior color, for instance, could possibly bring an increased price for the product—or less sales resistance.

In many applications, conventional approaches require so much sophistication that they are often more expensive than thin-film evaporators. Examples of this are the separation of fatty acids or fatty amines, and the removal of color from plasticizers. In the latter case, mechanically aided thin-film evaporation is almost mandatory; processors have found it the only suitable method for removing color to meet customers' specifications. It is virtually impossible to remove color from plasticizers by standard evaporation because of heat damage and decomposition resulting from the relatively long time the product must remain at temp. With a mechanically aided thin-film evaporator, the plasticizers can be exposed to higher temp for a relatively short period with no thermal degradation of the product.

Furthermore, some users have found that the unit, although purchased for a specific difficult process, also can be applied to conventional evaporation processes economically. The same unit used for separation of di- from triethanolamines can also be used to recover spent ethylene glycol or to strip unreactive materials from alkyl phenol.

Application Criteria

Thin-film evaporation should always be given serious consideration whenever the processor is dealing with materials that are heat sensitive, or viscous, or have low thermal conductivity. Typical examples are tall oil, fatty acids, rosin, amines, esters, rocket fuels, urea and other fertilizers, radioactive wastes, and fruit juices. The range of separation processes is extremely broad and includes dehydrating, deodorizing, decolorizing, stripping and concentrating.

Mechanically aided thin-film evaporation is relatively new. Hence, compiling a complete formal set of criteria for application of thin-film evaporators is difficult. However, a good basic knowledge of the physical properties of the product may be all that is needed to decide whether or not thin-film evaporation should be used. Let us consider the effect of heat transfer, feed rate, viscosity and vacuum on thin-film evaporators.

Heat Transfer Rate. Extremely high heat transfer rates are characteristic of these units. In fact, overall heat transfer coefficients as high as 3750 BTU/hr/sq ft/°F have been reported. Such values are atypical and result from controlled conditions with special experimental apparatus which has an extremely thin heat transfer shell. More common values range from 350–450 BTU/hr/sq ft/°F for water-like products in production equipment with a heavier gauge wall that provides structural rigidity and strength to withstand high jacket pressure. With viscous products, the inside shell coefficient usually is the most important factor in determining the overall heat transfer coefficient. Reducing film thickness increases the film coefficient. A major consideration, therefore, in the mechanical design of thin-film evaporators is how to produce a thin, evenly spread film which moves rapidly across the transfer surface.

Conductivity of the barrier wall is also a consideration. Most large size stainless steel units are clad with carbon steel to take advantage of its higher conductivity. Also, spirals in the jacket are often used when the heat transfer medium is either hot water, Aroclor, hot oil or liquid Dowtherm.

The high heat transfer efficiency of the mechanically aided thin-film evaporators makes them ideal for handling products that have low thermal conductivity. This is the type of product that might be more economically handled in a thin-film evaporator than in a standard type evaporator (even though the latter may be able to handle it) since overall heat transfer and ultimately the output will be greater in the thin-film type. Examples of products with low thermal conductivity that can be handled by thin-film equipment include fatty acids, ethanolamines and urethane polymers, or in general those materials whose thermal conductivity is 0.08 BTU/hr/sq ft/°F/ft or less.

High heat transfer is also the principal reason for the ability of mechanically aided thin-film evaporators to handle heat sensitive products. Another reason is the rapid movement of the product over the heat transfer surface. In most thin-film units the product remains in contact with the heat transfer shell for a very short time. This contact time varies from one sec up to a maximum of approx five sec, depending on the viscosity of the material. Thus, time at temp of the product is minimal compared to conventional techniques. The time at temp for a product being handled in a conventional evaporation such as a calandria can seldom be determined because of the constant recycling of the material. Most thin-film evaporation is a one-pass operation.

With heat-sensitive products, the time that a product can remain at a given temp without degradation is usually known, or should be known. If laboratory work has been done on the product, the time-temp relationships undoubtedly have been established. When normal evaporative methods exceed or approach this critical temp, mechanically aided thin-film evaporation should definitely be investigated. It must be remembered that decomposition is a function of both time and temp, and in many cases, a well-established (by normal standards) decomposition temp is greatly exceeded by thin-film processing without degradation. This, of course, is due to the short contact time with heat. A further benefit derived from higher temp operation is a reduction in the viscosity of the material being handled.

Feed Rate. The mass flow rate of feed is one of the variables affecting the thickness of the film obtained. Feed rates vary with unit size, evaporator length to diam ratio, percentage of distillate desired from one pass, jacket temperature and physical properties of of the feed.

Evaporation rate varies from feed rate. At low rates there is insufficient wetting of the heated surface, resulting in a dry wall effect and low evaporation rates. As the feed rate is increased, the evaporation rate increases up to a maximum; when the feed rate is increased beyond this point, the film thickness increases causing the evaporation rate to decrease.

Viscosity. The more viscous the material, the greater the difficulty in thinning, spreading and depositing the film. Nevertheless, thin-film equipment is probably the most effective method for evaporating highly viscous products. Materials whose residue viscosities are in the range of 100,000 centipoises—e.g., tars remaining from tall oil processing—have been processed with good results.

For a given product, viscosity varies at different points along the length of the evaporator. At the top of the unit, fluid consistency is low, rate of evaporation is high. At the bottom, high product consistency and low evaporation rate result in a low film coefficient. Overall film coefficients are the average of these extremes and intermediary points.

Water or water-like products are distilled by thin-film equipment at maximum rates of ca. 50 lb/hr/sq ft. For low viscosity organics with a low latent heat of vaporization, distillate rates up to 100 lb/hr/sq ft have been obtained. Examples include desolventizing ethylene glycol or rocket fuels. On the other hand, high viscosity products exhibit distillate rates in thin-film equipment as low as 10–20 lb/hr/sq ft, i.e., desolventizing urethane polymers.

Of course, whether or not a fluid is Newtonian or non-Newtonian—i.e., thixotropic, pseudoplastic, dilatant, etc.—should be taken into consideration. Shear rate vs. shear stress values can be an aid in determining the need for thin-film equipment.

For a normal Newtonian fluid, thin-film evaporators should always be considered whenever the viscosity of the residue approaches 20–30 centipoises and above, but a great many applications have proven to be economically feasible even with viscosities that are only 3.5 centipoises.

Vacuum Operation. Vacuum also controls heat transfer rates in thin-film equipment. Standard thin-film evaporators usually operate at internal pressures from 0.3–20 mm Hg absolute.

In several types of thin-film units (those with external condenser), there is little to be gained in terms of reducing boiling point by operating at pressures lower than approx 4–5 mm Hg absolute at the evaporator. This is because of the pressure drop which occurs from the external condenser to the evaporator. Thin-film evaporators equipped with an internal condenser on the other hand, keep pressure drop between evaporator and condenser at a minimum. With an internal condenser it is possible to distill many fringe products for which higher vacuum, if not actually needed, is more efficient and economical.

Future

Widespread use of thin-film evaporators is certain. For many problem products there is no effective alternate processing method. As news of successful applications becomes more widespread, there will be a further impetus to the adoption of this technique.

Manufacturers have demonstrated the importance of time as a controlling factor in the operation of thin-film evaporators. Higher temp than once thought possible can be utilized because average retention time is low, due mainly to one-pass operation. However, user understanding of the relative importance of time vs. temp in thin-film lags considerably behind demonstrated equipment capability. The need for better processing methods should spur producers to master the techniques of using thin-film equipment.

Manufacturers are continuing their evaluation of performance and are making further improvements. Both factors in the time-temp relationship are the subject of study at the present time. Heat transfer will undoubtedly receive more attention. Improvements depend on the advent of readily available and economical clad materials such as copper-clad stainless steel. Further work has focused on jacket design to improve heat transfer. The use of spiral jackets is a step in the right direction, but the use of stiffening bars or some variation of dimpled jackets may eventually lead to the use of thinner shells for better overall heat transfer.

Another limiting factor in the design of these units is conc removal. Advances in this area will require the development of improved pumps and new designs for outlets, to keep the highly viscous conc moving. Mechanical design considerations relative to the rotor design will also be studied.

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