VISIT BY MR. F.W. WAINEWRIGHT TO THE ROOKERY BRIDGE REFINING CO., LTD., ON 19TH - 20TH MARCH, 1963.

This Member was having deliveries of hot bone glue solution rejected by a customer. The complaint was principally of the bad odour of the glue although loss of physical properties had also been mentioned. The visit was made, therefore, to inspect the manufacturing plant for sources of contamination, and to make recommendations of methods to overcome or avoid the contamination.

It was learned that the deliveries were of a non-foaming type of bone glue. The "Bevaloid" defoamer manufactured by Richard Hodgson & Sons, Ltd., was being incorporated, after the dilute liquid had been concentrated to 58%. A delivery varied from 2 to about 4½ tons, usually being the larger amount as this was more economical to transport. Delivery was being made by a stainless steel tank mounted on a lorry. The temperature of the glue solution in the tanker, prior to delivery, was about 130°F (55°C) and, on reaching the customer had dropped to about 125°F (52°C). Maximum temperatures reached at the customer's plant was 170°F (77°C). Besides the defoaming agent, preservatives had been added to the glue. These included "Embatex", a solution of the sodium salt of Dichlorophene, manufactured by May & Baker, Ltd., and "Santobrite" (sodium penta-chlorophenate). Hydrogen peroxide was also added, primarily as a bleaching agent.

Glues can be degraded by four methods :-

I. Heat, which affects both the Bloom and viscosity of the product. Higher temperatures will cause more rapid degradation than low temperatures. It is preferable to keep temperatures below 60°C if possible. Above 60°C, thermal degradation becomes severe.

II. Chemical Action. A good example of this is the loss in viscosity of products caused by hydrogen peroxide. Again Bloom strength is also affected. Total degradation and also the rate of degradation will increase with increasing peroxide concentration.

III. Bacterial Degradation. This leads to complete loss of physical properties and bad odours. Bacterial attack can be inhibited by the use of bacteriacides, such as those which you are already using. Care must be taken in their selection, those with strong phenolic smells are unsuitable for uses such as gluing food-stuff containers or cigarette cartons. Similarly, very

poisonous preservatives such as phenyl mercuric acetate, could not be used in glues supplied to the gummed paper tape industry. Embatex is a particularly suitable preservative. It does not have a strong phenolic odour which will contaminate food-stuffs. It is also prescribed for the treatment of tape-works, in fairly large doses, so obviously it would be suitable for use in glues prepared for the gummed paper tape industry. Unfortunately, bacteria are able to acquire immunity to bacteriacides, if used constantly. It is possible, therefore, to build up bacterial strains on a glue making plant resistant to the particular preservative which you are using so that the glue degrades as rapidly as if no preservative had been used. One has, therefore, lost the price of the glue and also the cost of the preservative. To overcome this difficulty it is wise to vary the preservative being added at regular intervals, say, every two weeks. Similarly, the same techniques should be applied to the bacteriacide used when washing the plant through. Dilute hydrogen peroxide and dilute sodium hyprochlorite solution can be recommended for this purpose. Heating glue to a suitable temperature will also destroy bacteria, of course, but this will also cause thermal degradation.

IV. Enzymic Degradation. Emzymes arise from bacterial action upon glue and once again their presence in glues can lead to extremely rapid degradation and bad odours. It is difficult to inhibit enzyme activity; some are inhibited by acid or alkaline conditions, but as enzymes are themselves proteins, it is not difficult to see that conditions which will inhibit them will also cause degradation of the glue. All enzymes are destroyed by heat, but this again leads to degradation of the glue. It is thus obvious that to prevent enzyme contamination of glues it is necessary to prevent bacterial attack, by adding preservatives to the glues and scrupulous attention to plant cleanliness. Once bacterial attack has taken place in a glue solution then enzymes will be formed. Addition of preservative will destroy the bacteria but not the enzymes, and the glue will still degrade rapidly. Similarly, if glue becomes contaminated in the plant, say in a pipe which does not empty properly, and large quantities of enzymes are produced before the next batch of glue is pumped through the pipe, then even if the next glue batch has been properly preserved, it will still be enzymatically contaminated from the residue in the pipe and willbegin to degrade rapidly.

On considering the manufacturing process of your plant and taking account of the foregoing survey of the causes of degradation it is possible to pinpoint probable sites at which bacterial and/or emzymic contamination can occur and the precautions necessary to avoid such contamination.

First, most fresh raw material is beginning to decompose to a certain extent by the time it reaches the works. If care is taken to minimise the time that the raw material is held before processing then the decomposition of the raw material will be minimised. This will have a direct bearing upon the free fatty acid content of your greases, and to a much smaller extent the quality of your bone glue. But the more important factor is contamination of your glue from the raw material by flies and other insects. To avoid this it is necessary to cover all open tanks, such as the dilute liquor tank and the header tank of your evaporator. The only snag with covering such tanks is that the cleanliness of the interiors then tends to be forgotten. A regular inspection procedure should overcome this however, and this should preferably include the undersides of the lids which also tend to be forgotten.

As has been stated, heating will destroy bacteria and enzymes. The bone glue process is, therefore, particularly fortunate in the aspect that the product coming from the autoclaves is bacteria and enzyme free. All contamination present in the raw material before processing will be destroyed by your steaming procedure of 20 minutes at 20 lbs./in.^{2} process before hot water extraction. Therefore, if a preservative is added to the dilute liquors immediately they are blown from the autoclaves, then providing the remainder of the plant is clean the glue cannot be infected and must remain a stable product. During my visit I suggested that SO_2 gas could be used. This, if utilised to bring the acidity of the dilute liquor down to about pH 5.0 will have the advantage of bleaching the glue besides rendering it resistant to bacterial attack. During evaporation the acidity of the glue will fall a little further. As your dilute liquor is approximately 8-9% and you are evaporating to 58% it will probably drop to the region of pH 4.3 - 4.4. There are disadvantages in this system: (1) Dilute liquor will have to be held in the tank whilst the SO_2 is being added. This could be somewhat overcome by the addition of the gas whilst the liquor is being blown into the tank. (2) Some supervision of the acidity of the liquor will be required during the addition of the gas. This will require a workman's time. This difficulty could be overcome by

the addition of sodium metabisulphite instead of SO_2. Sodium metabisulphite releases SO_2 in acid solution, so that the acidity and bleaching effects of the gas are retained. Also, being a solid, it could be weighed into the dilute liquor or dissolved in a small amount of cold water and added to the liquor. The weight to be added can be calculated to give any desired SO_2 content than a table made up so that all that the workman has to do is measure the depth of glue in the dilute liquor tank (this will give the volume of dilute glue solution) and the concentration of the dilute liquor. From these two readings he can read from the chart the amount of metabisulphite he has to weigh out and add to the glue solution. Then the acidity of the glue should be adjusted to pH 4 with dilute hydrochloric acid which should not take long. The only snag here is that the addition of metabisulphite will increase the ash content of the glue slightly. I do not know if your customer is particularly fussy regarding this point. The other disadvantage is that you will be processing an acidic glue liquor and care must be taken that the liquors are not allowed to become too acidic or severe corrosion of your pipe-lines and evaporation plant may result. As your evaporator is copper tubed, there should not be much risk to the tubes, but the end iron plates may suffer.

If it is considered that the danger of plant corrosion is too great to entrust the use of SO_2 to a workman, at that stage, then one of the preservatives which you are already using can be added. If this procedure is adopted then some thought must be given to the method of controlling the level of preservative added. If the present technique of leaving about 15" of glue liquor in the dilute liquor tank is retained then either allowance for the amount of preservative present in the retained liquor will have to be made or two tanks should be installed, so that one tank can have its preservative added and then be drained while the process is being repeated on the other tank.

Whichever of these methods are adopted, and it is strongly advised that a preservative is added to the dilute liquor directly it is blown from the autoclaves, care must still be taken to keep the plant absolutely clean. It has already been stressed that no matter how well preserved the glue may be, if enzyme contamination occurs then the glue will degrade rapidly.

Therefore, it is advised that the wooden dilute liquors tank should either be scrapped and replaced by a metal one, preferably aluminium or stainless steel, or that the tank be lined, say, with polythene. The names and addresses of firms which undertake tank lining with polythene are as follows :-

Messrs. J. Currie & Sons Ltd.,
Parkgate Works,
Bank Street, Clayton,
Manchester 11.
Telephone : Man. East. 0247.

Messrs. Robert Jenkins & Co. Ltd.,
Wortley Road,
Rotherham, Yorks.
Telephone: Rotherham 4201

Messrs. W.G. Jenkinson, Ltd.,
156 Arundel Street,
Sheffield, 1.
Telephone: Sheffield 27438.

Messrs. Matthew Hall & Co. Ltd.,
101 Tottenham Court Road,
London W.1.
Telephone: Museum 3676

Messrs. Rediweld, Ltd.,
25, Kelvin Way,
Crawley, Sussex.
Telephone: Crawley 25692

Messrs. Tanks and Linings Ltd.,
Town Wharf,
Droitwich, Worcs.
Telephone: Droitwich 2240.

Messrs. Vicsons Ltd.,
148 Pinner Road,
Harrow, Middlesex.
Telephone: Harrow 0706

Naturally the cost of tank lining will depend to some extent upon the thickness of the lining used. It would be best to obtain the various firms recommendations on this point, but it should be mentioned to them that the tank will periodically be washed with hot dilute peroxide of hypochlorite solution. Covers for all tanks have already been recommended. As additions to the dilute glue liquors are to be made then some provision for access to the tank will have to be made in the lid, say a small flap. If this method is adopted then care should be taken that the lid of the tank is kept clean so that dust cannot fall into the glue liquors as the trap is opened. Similarly, old sacks should not be allowed to lie across the tank as they are at present.

Going from the dilute liquor tank to the evaporator, there is the header tank, which is of the ordinary galvanised type, and very rusty inside. Again, this tank could not be adequately cleaned and should be replaced. A further reason for replacing this tank is that if the SO_2 method of processing the dilute glue is used then the acid liquors will tend to dissolve rust, which will colour the glue. Thus the bleaching benefits of the SO2 treatment will be lost. Again the tank should be covered. The pit at the bottom of the old kestner evaporator, which is allowed to fill with stagnant water should be filled in. This is also a very likely point at which contamination could arise.

The concentration of 58% which your customer requires appears to be close to the limit of your two-stage evaporator. To achieve this concentration the evaporator is necessarily working under the rather low vacuum of eleven inches of water, and the glue has to be retained in the evaporator for an excessive time. This will cause thermal degradation of your glue. As mentioned during my visit, if the high concentration is necessary to give a required viscosity in your customer's formulation, then it is possible to increase the viscosity of your glue by a cross-linking method, so that you do not have to evaporate to such a high concentration. There are several points to be taken into consideration however. As mentioned, really high-speed stirring is necessary in some cross-linking reactions to prevent the initial high concentration of reagent cross-linking the glue excessively. If this occurs then the glue will contain insoluble particles which would be unacceptable to your customer. Formaldehyde has also to be used with care, otherwise the reaction tends to proceed further during the drying process so that your customer would end with a non-sticky tape. It may be possible to utilise sodium carboxy methyl cellulose, this would only entail adding the correct amount to your glue but again care will have to be taken that the "tack" of your customer's gummed tape is not appreciably affected. For the present it is probably wise to settle the degradation problem, while the viscosity problem is examined further here. In this way we shall be sure that the cheapest and easiest method of increasing the viscosity of your glue is found. In the meantime, it can only be stressed that the time at which the glue liquor is held at temperatures of 60°C (140°F) and above should be kept as short as possible, both at your Works and your Customer's Plant, and that in any case the temperatures should be kept to a minimum. Similarly, the glue delivery should be used as quickly as possible. Your customer's practise of holding glue liquors over from Friday until Monday, even under mild heating conditions, will undoubtedly lead to thermal degradation. Arrangements should be made either to use the glue completely by Friday evening or, if this is difficult, to allow the glue to set and remelt early on Monday morning.

There remains only general points of plant cleanliness. Besides.....

keeping the tanks clean, it is necessary to make sure that tank stirrers are also clean and free from rust. This applies also to the filter boxes placed across the tanks, and the guttering used to lead the glue liquor from the outlet point across to the galvinised tank standing by the side of your two stainless steel becks. I mentioned that it was possible to obtain synthetic resins with which to paint the inside of the galvanised concentrated liquor tank, which is showing signs of rust. A firm which can supply such materials are :

Messrs. Devroome Developments Ltd.,
31 Friern Barnet Road,
London N.11.
Telephone: Enterprise 8441.
Mr.J. Hayes is the Chief Chemist.

Also all hydrometers which are used to test the glue concentration must be kept clean. The hot water baths to the stainless steel becks should be periodically drained so that contamination of the concentrated glue from dirty bath water cannot occur. One final point: All pipework should be examined to make sure that glue liquor is not trapped when the system is drained. If material is trapped, then once it becomes contaminated by a batch of infected glue being processed, material always remains to contaminate subsequent batches.

The use of SO_2 in place of hydrogen peroxide as a preservative and bleaching agent has already been recommended, and control of the acidity of the glue solution mentioned. A cheap and simple method of checking the acidity of the liquors, which can be used by relatively unskilled labour is the Lovibond comparator, which compares the colour produced by a mixture of the glue liquor and an indicator solution against a standard colour disc. This can be purchased from Messrs. Griffin & George, Ltd., Ealing Road, Alperton, Wembley, Middlesex. The apparatus required (and Griffin and George's catalogue No's.) are as follows :-

Lovibond comparator S19 -720	£2. 17. 6d. (prices approx. in 1962).
Test Tubes (two at least required) - S19 732/30 each	3. 0.
Two comparator discs, (one wide range, one narrow range) - S19 732/18 2/100 B.D.H.	4. 4. 6.
2/1D B°D°H°	4. 4. 6.
The correct indicator is supplied with the disc.	£11. 12. 6.

Mr. Searle also mentioned, during my visit, the possibility of your laboratory commencing viscosity determinations. During the discussion a unit was mentioned which has only to be clamped to the side of a glass bath to give a reliable and accurate viscosity bath. This is the "Temp" unit, which combines heater, water circulator and thermostat, and is probably the cheapest method of obtaining a temperature controlled bath. For the glass bath it is possible to use battery jars. Viscometers will also be required, and these can be obtained from Messrs. Griffin and George whose address is given elsewhere in this report. The type C Ostwald Viscometer of B.S.S. 188 (1957) is the one required (G. and G. Catalogue No.L26-905) together with viscometer holders which can be obtained from Townson and Mercer Ltd. Croydon. Catalogue No. B.S. 127L. The viscometers we will calibrate for you. The Temp unit can be obtained from Techne (Cambridge) Ltd. Duxford, Cambridgeshire.

Besides the routine determination of viscosity, the viscometers can also be used to determine whether bacterial or enzymatic contamination of your products has occurred, by measurement of the product's stability. Then by taking samples at each stage of your manufacturing process say, liquor from autoclaves, liquor after concentration, liquor from the tanker, and finally a sample after reaching your customer's plant, the point at which contamination occurred can be found and the appropriate action taken. The method of determining viscosity stability is given in the article by Kragh and Langston Bulletin Vol. 10 (1959) No.4. If your copy of that Bulletin is mislaid a spare can be supplied.

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