15.0 Review of work done for making crude sugarcane wax to an industrial quality wax:

From the industrial processing point of view, the physical and chemical properties of the better quality wax is superior to crude sugarcane wax. Crude sugarcane wax has not been found to have sound footing for the industrial application in mass scale in polish, carbon paper, printing ink, lipstic, electrical insulation, solid floor wax, wrapping or packaging foods, coating for chocolates, leather polishes, moulds, dental wax making etc. on account of certain inherent physical and chemical characteristics. All these applications require wax having specific quality and property suiting to the desired products.

Crude wax, as obtained by solvent extraction of press mud, is not generally suitable for commercial applications because of its variable comosition and undesirable characterstics. It is greenish black in colour, soft and has a high ash content. It cannot be directly consumed in industry as it is liable to bloom, sets improperly in pastes, and has dark colour and objectionable odour. It is sticky and due to takiness, it produces difficulties on onward processing in industrial applications. The solvent retentivity power also varies as compared to camauba and other waxes available in the market. In order that it may be acceptable for all industrial applications, it must be subjected to refining/ chemically modified so that sugarcane wax could be a possible substitute for camauba wax and other imported wax. However, to produce hard wax from crude sugarcane wax, it is essential to remove the undesirable constituents which involve further
solvent extraction technique inter alia would incur more expenditure increasing solvent and material loss leading to ineconomy.

The importance of waxes in industry has increased greatly during the past so many years. Waxes possessing various well defined and uniform properties are required for many purposes apart from the obvious uses of waxes in making polishes. Hence for all practical purposes hard wax of having high melting point is required. During the past a considerable amount of work has been done on refining of cane wax and numerous refining methods have been developed. These methods may be classified into two groups, one of which consists of treating of crude wax without prior removal of fatty fraction, and the other of treating the dark hard wax obtained from crude wax. These methods have not met with much success as it has been found that sugarcane wax is much resistant to usual bleaching agents.

Balch and Broeg 78 hold the view that this resistance indicates the presence of at least two components in wax. Hence it has been concluded that successful refining would depend upon fractionating in some manner.

W.G. Cass 79 holds the view that the crude wax obtained by extraction of filter press mud with petroleum solvent could be purified by crystallization or by fractional distillation. Wax obtained by crystallization from petroleum could be bleached with chlorine or with potassium chlorate and sulphuric acid.
Rao and Vidyaithi observed that crude wax obtained by benzene extraction, could be purified by boiling with sodium sulphate solution and then with carbon tetrachloride solution at pH 7.5 - 8.0. However, above purification did not remove soft fatty matters.

Gilmore's process consists in boiling a suspension of crude wax in dilute acid which removes basic impurities and inorganic constituents. The wax thus obtained was washed with water to remove acid and after drying, the wax was extracted with ethanol to remove soft fatty matter. Latter the wax was bleached by means of potassium chlorate and sulphuric acid.

Balch and Balch and Broeg devised a method whereby crude wax, first broken up into small flakes. It was then extracted with cold acetone in order to dissolve out soft fatty substances. This requires considerable time and alternative procedure is to add acetone, filtered and cooled concentrated benzene extract of filter press mud. In this way pure wax is made by crystallizing out from solvent mixture.

Broeg, Charles B and Balch found that two alcohols, ethanol (anhydrous) and 2-propanol (95 - 99%) give satisfactory results. In this method of refining, the dark hard wax was digested with about five parts of alcohol at boiling point of the solvent until equilibrium was established and the clear solution was decanted from insoluble fraction. The latter was digested several times again with about one part of alcohol per cycle in a similar manner. The extracts were then combined, treated with decolourising agent and filtered. The wax was recovered by distilling the
solvent. The products from this refining method were claimed to be (i) light coloured hard wax (ii) dark coloured alcohol insoluble fraction or pitch.

Gundurao et.al in their experiments to improve the hardness and colour of crude wax attempted (i) fractionation by selective solvents (ii) fractionation by settling (iii) extraction of press mud in cold (iv) refining by chemicals and otherwise. In (i) they had tried to separate hard wax from fatty portion by selective solvents like acetone, ethanol, petroleum ether, solvent oil and turpentine (mineral), all used in cold.

Acetone and alcohol were found to be the best solvents for fats. Results obtained with selective solvents are given as under:

Table-XXXI

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<thead>
<tr>
<th>Solvent</th>
<th>Hard wax % crude wax</th>
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<tbody>
<tr>
<td>1. Acetone (cold)</td>
<td>60%</td>
</tr>
<tr>
<td>2. Alcohol (cold)</td>
<td>60%</td>
</tr>
<tr>
<td>3. Petroleum ether (cold)</td>
<td>35%</td>
</tr>
<tr>
<td>4. Solvent Oil (cold)</td>
<td>52%</td>
</tr>
<tr>
<td>5. Mineral Turpentine</td>
<td>50%</td>
</tr>
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In (ii) they had tried fractionation by fractional crystallization. Hot concentrated extract of press mud in solvent was followed to cool when wax
separated and settled in to a separate layer, the supernatant liquid containing most of the fatty portion and a much smaller content of wax.

In (iii) the press mud was first extracted in cold followed by hot extraction giving hard wax.

In (iv) experiment, they had tried to modify the fatty portion in crude wax without separating it (i) by use of high pressure steam for some time in the still after the solvent was distilled. This treatment was found to bring about partial decomposition of fatty portion and thus hardening the wax, (ii) by initial fermentation of mud itself before drying. These treatments were followed by bleaching of hard wax with oxidizing agents like nitric acid, hydrochloric acid, cold chromic acid, potassium chlorate and sulphuric acid, sulphur dioxide, chlorine with carbon. Nitric acid and potassium chlorate with sulphuric acid has been reported by them to give the best results.

Shear 85 in his experiment de-ashed wax by boiling with sufficient normal (or more dilute) hydrochloric acid to have sharp separation of wax and water layers. Wax was fractionated into hard wax soft fatty potion by crystallization from its solution or other solvent, adding acetone, filtering and washing the wax crystals with acetone till the filtrate is clear. Powdered wax thus obtained. Attempts were made with ethyl alcohol for fractionating both in hot and cold. Hard wax thus obtained subjected to bleaching with potassium chlorate and sulphuric acid. Light brown to chocolate coloured wax was obtained.
Swanson 86 carried out experiment for purification of wax already freed from soft fatty matter with a fat solvent and heating the mixture under pressure to such a temperature in which wax dissolves and leaves resinous mass behind. Crude wax thus obtained was melted and mixed with 1:7 parts acetone, methyl ethyl ketone, ether, hexane or heptane at 100 °C under pressure and injected into a vessel (with stirrer) containing a slurry of wax in not less than 4 parts of solvent at 25 – 30 °C, under reflux and 200 mm pressure. The hard wax fraction was instantaneously precipitated and removed by filtration.

Mc Cloud 87 used isopropyl alcohol as solvent. This method had the advantage that the use of pressure higher than the atmospheric pressure need not require to apply during purification, boiling point of the solvent being above the melting point of wax.

Wilder 88 put forward a method for purification of wax both from fatty and resinous matter. This method consisted of melting the crude wax at 95 – 90° C. The molten wax was poured into a fat solvent maintained at 35 °C with agitation. After 15 minutes further stirring, the solution containing the hard wax was filtered. The pouring qualities of the wax (molten) was improved by addition of benzene, toluene or xylene to the extent of not more than one part to fifteen parts of wax. The solvent specified was acetone or methyl ethyl ketone but also may be ethyl ethers, heptane and pentane etc. The ration of solvent to wax 2- 4 : 1 and preferably 8:3.

Davison and Wiggins 89 used alcohols like ethyl, isopropyl and iso or n-amyl alcohols for refining crude wax. These alcohols dissolved
hard wax and fatty matter when hot but not resinous impurities. On cooling, hard wax alone was crystallized out. Colour could not be removed by this method. It was observed that colour could be removed if bentonite is mixed with crude wax and isopropyl alcohol as solvent and the mixture is filtered. However, a suitable refining solvent was found to be fused oil (essential mixture) of amyl, isoamyl, propyl and ethyl alcohols with some water and fatty acid esters.

Hixon and Miller\cite{90} developed a method for refining of cane wax which consists of fractionating in a continuous liquid-liquid extraction system with liquefied propane. In this method, the crude was melted and pumped into extraction tower near top. Liquefied propane is pumped near the bottom. The propane is maintained at 180 °F at the top of the tower, the temperature being less in lower section of the tower. The pressure in the tower to keep propane in the liquid state should be 80 lbs above vapour pressure of propane. The colouring matter and insoluble constituents of crude wax fall to the bottom and were drawn off at the base of tower, the solvent containing the remainder of material is drawn off from the top. Each portion flows to a unit for solvent recovery. The dissolved fraction yields a light coloured wax still contains fatty material. Further separation could be done by cooling the propane solution at 50–100 °F whereupon wax crystallizes and fat and residual colouring matter remain in solution. Hard wax is separated by filtration or centrifuging and the remaining solution is sent to the solvent recovery unit. The solvent crude wax ratio for simple separation of colouring matter may be 15:1 by weight. For full extraction with fat, separation ratio 20:1 is suitable. Other liquefied gaseous paraffins may also be used like ethane, butane or mixture.
All these methods preparing purified hard sugarcane wax so far mentioned have entailed (i) the extraction of crude wax with one solvent (ii) the purification of crude wax by treatment with a different solvent, but several processes have been devised whereby a pure wax may be obtained directly from filter press mud by use of one solvent. One of these methods is due to Goefort. In this method, crude wax is extracted from press mud with hot isopropyl acetate then, on cooling the filtered solution, hard wax crystallizes and may be separated from the soft fatty materials remaining in solution by filtration. The main objection to this method however, is that the solvent is an ester and may well tend to hydrolyse during extraction, thus forming acetic acid which would not only lead to loss of solvent, but also to possible deterioration of the wax. Further more, isopropyl acetate is a very expensive solvent.

Sklar developed a method for extraction of hard wax from press mud with liquid sulphur dioxide under pressure. Although this is said to be successful, the cost of pressure equipment and the cost of skilled operators required to handle it might well outweigh its advantage.

Merz has developed a method of obtained pure wax by use of one solvent. The principle involved in this procedure is that dry filter mud is extracted twice under different conditions with a petroleum solvent which is composed of essentially heptane. This first extraction is carried out with boiling solvent and this extracts the hard wax. In this process no filtration operation is required, but on the other hand, a refrigerator is need in a tropical climate to cool the solvent to 15-18°C for fat extraction. If warm solvent is used that would extract the wax also in first extraction and hence
is lost. Another disadvantage of this method is that complete extraction of mud takes at least twice as long as crude wax extracted by ordinary method and produces lower yields of pure wax than are obtained by double solvent processes. Furthermore, this process does not remove the resinous fraction from the hard wax.

Methods so far adopted by various authorities have fractionation by some process of solvent extraction (whether one solvent or two solvents) as their basis. It seems desirable to consider the merits of methods which avoid the use of organic solvent. Wijnberg 94 tried to refine wax under reduced pressure by distillation of the whole wax. The results were disappointing.

Distillation methods of refining wax have been described by Wiggins 95 and by Hatt et. al 96. Both the two workers have found that cane wax may be distilled under a high vacuum and that it will distil in steam. The wax can be separated by distillation into two fractions, a distillate which is soft and pale yellow mainly containing components of low molecular weight, leaving the desired hard wax as residue. Steam distillation also purifies cane wax but has poor yields with high distillation losses. Nevertheless, high vacuum distillation of wax is commercially possible but is in no way economical.