

Plasticizers for Cellulose Acetate

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CELLULOSE acetate, the ester of cellulose and acetic acid, is obtained by treating chemical cotton or bleached sulphite pulp with acetic acid and acetic anhydride, in the presence of a catalyst like sulphuric acid. The initial product is the triacetate or primary acetate, having an acetyl value of 62.5% ; this, however, has not become industrially important because of its limited solubility in the common nontoxic solvents, restricted compatibility with plasticizers and poor thermal and flow characteristics. It is however produced as an intermediate, in the manufacture of commercially-useful, solvent-soluble secondary acetates which are produced by the partial hydrolysis of the primary acetate. The solubility characteristics of the triacetate can be improved if a portion of the combined acetyl groups is hydrolysed, to leave a degree of substitution of about 2.5. If substitution is further decreased, solvents of greater polarity are required until at a substitution of about 1, the product becomes water soluble. For use in plastics, cellulose acetate having an acetic acid content of 52 to 54% is preferred, while for use in surface coatings 54 to 55% acetic acid content is found to give the best results ; for films, sheets and foils cellulose acetate having 56 to 57% combined acetic acid is used. Briefly, the various steps involved in the manufacture of cellulose acetate are: (1) swelling the cellulose with glacial acetic acid, (2) esterification with acetic anhydride, in the presence of a catalyst which results in the formation of triacetate, (3) hydrolysis of the triacetate with water, (4) washing, stabilizing and drying of the secondary acetate.

Even the secondary acetates, despite the improved properties, cannot be used

as such, except for the casting of films and foils. For use in moulded plastics or surface coatings, addition of plasticizers and/or resins is essential. The secondary acetate does not have sufficient flow even at elevated temperatures and will decompose if temperature is raised beyond 240°C. It is, therefore, essential to have recourse to plasticization in order that cellulose acetate can be conveniently moulded. It may be added that cellulose acetate has been described as the ideal material for injection moulding and injection moulding is ideally suited for cellulose acetate.

Plasticizers are defined as nonvolatile solids or liquids, which cause a change in the elastic properties of a resinous or macromolecular substance. Plasticized materials usually possess enhanced flexibility and impact strength but reduced modulus and softening point. In certain cases plasticizers can actually "toughen" the polymer, e.g., camphor and cellulose nitrate. In addition to the changes in elastic properties, certain other secondary properties like water absorption; resistance to solvents, stability to weathering, etc., are also affected.

Many theories have been put forward from time to time to explain the mechanism of plasticization. The first theory which received wide acceptance was put forward by Kirkpatrick¹ who visualized that one end of the plasticizer molecule was attached to the macromolecule, the other end of the plasticizer acting as a sort of lubricant between adjacent macromolecules. Clark² visualized the mechanism of plasticization as the filling of large voids in the molecular space lattice, thus forming planes of

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easy glide. Other investigators like Debell³, Barron⁴ etc. believe that plasticization involves freeing the adjacent chains of the macromolecule so that their segments can more readily slip past each other.

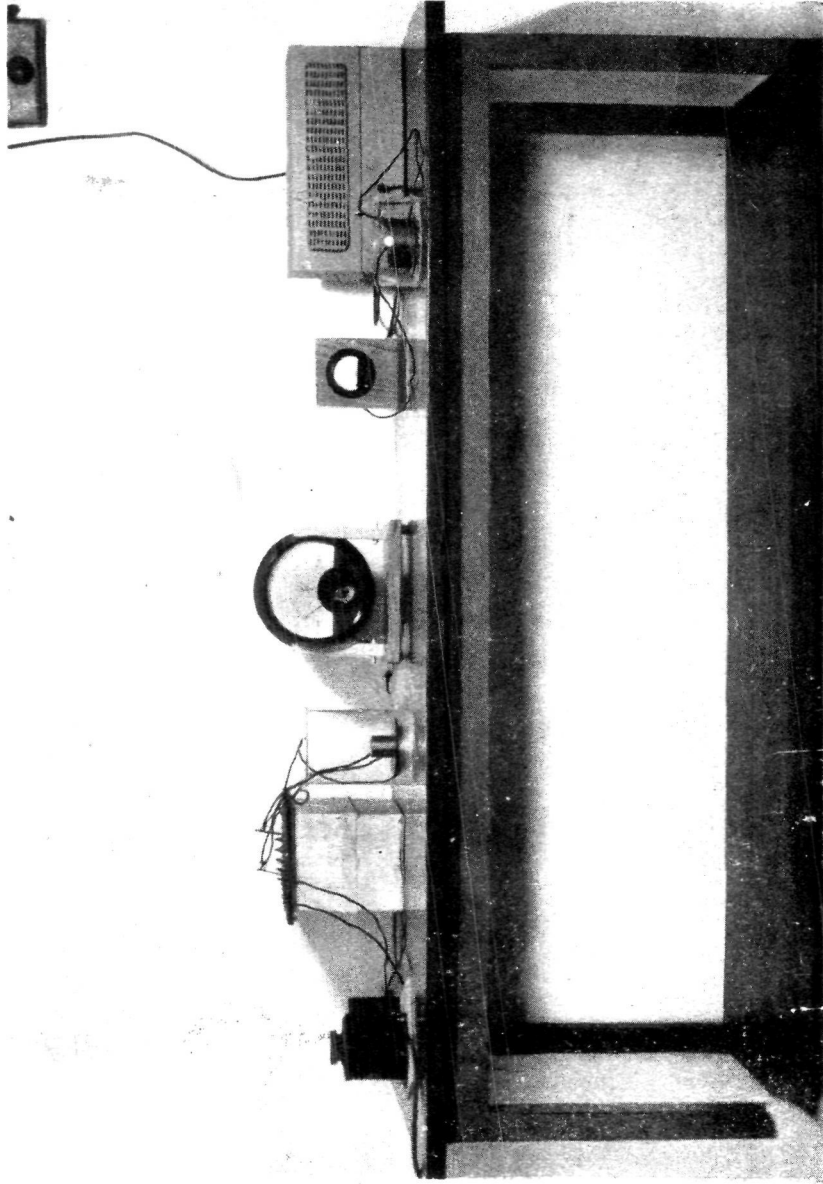
The modern trend of thought is towards the theory that an unplasticized plastic is like a three dimensional gel, the effect of plasticizer being to reduce the extent of the three dimensional structure. According to this theory an unplasticized mass is considered to be a closely packed three dimensional internal honeycomb structure, there being force centers on the macromolecules which are very close to each other and which are loosely attached. The movement within the mass is restricted so that any attempt to deform the material cannot be accommodated by movement within the mass. The action of plasticizer is to mask many of these force centers so that fewer force centers are left. The plasticizer molecules are not bound permanently. There is always a sort of competition between the plasticizer molecules and the active groups on the neighbouring macromolecules to secure a bare force center on a macromolecule, the number of force centers solvated being dependent on the strength of the forces of attraction and on the mobility of the plasticizer molecules. When a specimen is brought from a higher to a lower temperature, the specimen contracts, the molecules get closer together, the forces of attraction between the macromolecules become greater, the mobility of plasticizer molecules is decreased as a result of increase in viscosity, with the result that further desolvation takes place so that a greater fraction of the force centers on the macromolecules become attached to each other. This means that at lower temperatures, the specimen offers greater resistance to deformation and less resistance to fracture than at higher temperatures, or, in other words,

the specimen becomes more brittle and more stiff.

Plasticizers are classified into two classes, (1) true or solvent plasticizers or gelatinizers and (2) nonsolvent plasticizers or softeners. The solvent type is compatible with the resin or macromolecule in appreciable quantity and acts as a single, thermodynamically stable phase throughout; while a nonsolvent type of plasticizer has a tendency to separate as a different phase.

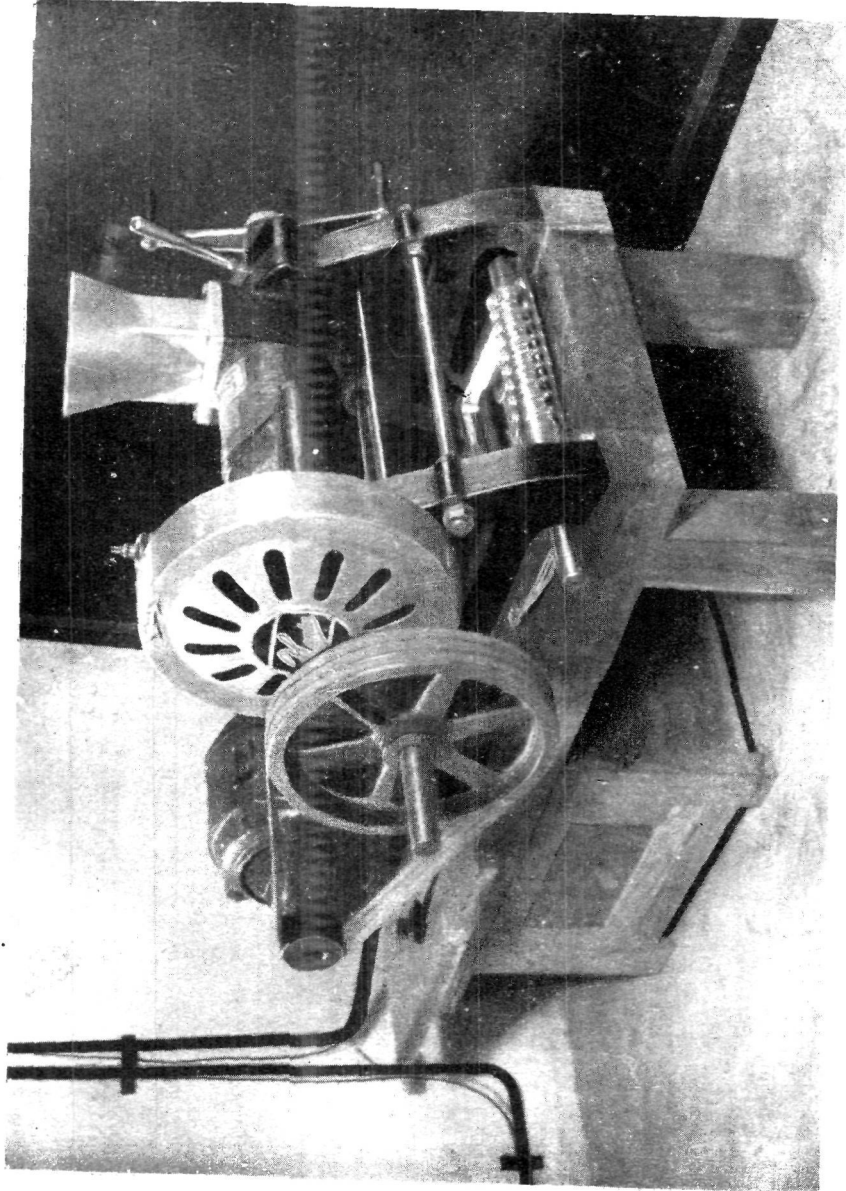
Whether any given material will act as a solvent or nonsolvent plasticizer will depend on the strength of the forces of attraction between the plasticizer and polymer molecules. Investigations of Gilbert and Gloor⁵ indicate that most true plasticizers for cellulose acetate are acetic or propionic esters of alcohols and methyl or ethyl esters of acids of low volatility with the carbonyl group arranged in a linear or planar relationship within the molecule. It is possible that amides of sulphonic and carboxy acids may also behave as true plasticizers provided the acyl-amido groups are in the same plane with the rest of the molecule. To some extent this is substantiated by the known plasticizing effect that is obtained with N-ethyl aryl sulphonamides and N-acetyl carbazole.

The choice of a plasticizer is made according to the service requirements of the final product. It is however necessary for a laboratory worker to determine as quickly as possible which of the plasticizer is suitable. The plasticizer must be compatible with cellulose acetate in appreciable quantity, must be retained throughout a reasonable period of ageing, must remain colourless and must not induce acidity in the composition. Some of the properties of technically valuable plasticizers are: (1) compatibility, (2) ease of incorporation and (3) permanence. In addition, physiological properties, economic and any other special factors have also to be considered.



EQUIPMENT FOR THE ELECTRICAL TESTING OF PLASTICS
(Paints and Plastics Section)

Photo by: C. B. WADIKAR



BABY OIL EXPELLER
(Cils, Fats and Waxes Section)

Photo by: C. B. WADIKAR

Compatibility is favoured by the presence of an adequate number and suitable distribution of solvating groups in the plasticizer. Incompatibility is manifested by exudation (spewing, sweat out or bloom) of the plasticizer from the plastic. Compatibility is determined by making films from cellulose acetate, containing increasing amounts of the plasticizer. After evaporation of the solvent, the quantity of plasticizer which gives a clear film gives the compatibility. The films are cured for about 18 hours at 55°C in an oven and the plasticizer content is determined by analysis. This gives the maximum compatibility. Ease of incorporation is only determined when the other factors are found to be satisfactory. The different methods of incorporation can then be tried on a pilot plant scale. Permanence involves volatility, resistance to water, oils and greases and chemical stability. Factors influencing volatility are vapour pressure, diffusion rate through the plastic, thickness, area of specimen, temperature, etc. Impermanence may result from chemical instability either by oxidation or hydrolysis to a less compatible, more volatile or more soluble product. Standard methods are available for the evaluation of the above factors.⁶

Physiological properties include odour, taste and toxicity. Since these factors are likely to affect the health of the workers, their determination is important. Information regarding these factors is usually given by the manufacturer of the plasticizer.

Of the two thousand or more substances which have been suggested as plasticizers for cellulose acetate—newer materials being added as a result of research—a good many have been found wanting because of their low compatibility, poor water resistance and high cost. In fact, it will not be an exaggeration to say that there is not a single true

plasticizer for cellulose acetate which meets all the requirements. For example, dimethyl phthalate is water-resistant but highly volatile; the glycolates toughen the product but are costly. In practice, therefore, mixtures of different plasticizers are used according to the properties required.

Cellulose acetate will undoubtedly occupy an outstanding position in the Indian Plastics industry as the basic raw materials required for its production are by-products of well-established agricultural products like cotton and sugar. As an injection moulding material, it finds competition from polystyrene. However, polystyrene has a tendency towards brittleness which can only be overcome by careful annealing of the moulded article. Also the softening point of polystyrene is low and use of plasticizers will further reduce it, thereby restricting its usefulness in tropical conditions. In case of cellulose acetate, the moulding strains are taken up by the plasticizers, the material itself being tough and hard. However, the use of cellulose acetate in plastics and, to a lesser extent, in surface coatings is dependent on the availability of suitable plasticizers in adequate quantities. Quite a few of these plasticizers can be made from indigenous raw materials, mainly of agricultural origin, and every encouragement should be given for their development.

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