Cellulose Triacetate for the Manufacture of Photographic Films

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History of Photography.
Manufacture of Cellulose Triacetate from Cellulose.
Casting of Film base from Cellulose Triacetate.
Different applications of Cellulose Triacetate base for other than Photographic Films.
Brief description of manufacture of Photographic Films.
Photographic Paper.

Photography is the process of producing a visible image upon a surface by the action of light or other radiant energy.

It was in 1839 that the first exhibit of a "photograph" came into being and this could be reckoned as its official birthday. From this modest beginning, photography progressed steadily and it was in 1889 that George Eastmen introduced the first transparent flexible photographic film base from *Cellulose Nitrate*. Following this development, Edison & Lumiere invented practical methods for producing motion pictures. Photography has undergone numerous refinements and to-day it is in a state of advanced technology.

The production techniques of manufacturing photographic films are quite complicated and shrouded in secrecy. The various steps in the manufacture of photographic films are production of base, photosensitized emulsion, coating of emulsion on the base and subsequent slitting, perforation and allied operations. Cellulose Nitrate was the first plastic material to be used as a base for photographic film in motion picture industry. The major disadvantage of this material was its high inflammability.

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In 1901 Baver & Co patented the casting of cellulose triacetate base from chloroform. In 1925-26 Bauchet & Co of France began casting of cellulose triacetate base using mixture of methylene chloride and methyl alcohol as solvents for cellulose triacetate. Its introduction to the market as transparent safety base (non-flammable material) replaced the use of highly inflammable cellulose nitrate base in motion picture industry. Cellulose Triacetate base is used in other fields of photographic industry for roll film, blue tinted x-ray films, grey tinted cinema sound negative films. HPF manufactures photographic film base from cellulose triacetate.

Cellulose is the most abundant and widely used natural polymer in the world, compared to the other two natural polymers Proteins and Rubber. There are two main commercial sources of cellulose i.e., wood and cotton seed hair. Cellulose is a Polyhydroxy alcohol confirming the existence of three hydroxyl groups for each anhydro glucose unit and these are the hydroxyl groups which can be esterified to get cellulose derivatives.

Cellulose acetate is the most widely known organic acid ester of cellulose. It is used for a variety of applications like cellulose acetate yarn, photographic films, transparent and pigmented sheeting, plastic compositions such as those used for compression, extrusion and injection moulding. Cellulose Triacetate is a fully esterified cellulose acetate containing 2.0 to 2.9 acetyl groups per glucose unit. Cellulose triacetate is manufactured by two processes namely solution process and fibrous process.

Solutions or Homogeneous process

The cellulose from wood pulp or cotton linters is usually given an activation treatment before acetylation by treating it with aqueous acetic acid. Activated cellulose is acetylated in presence of mixture of acetic acid and acetic anhydride using sulphuric acid as catalyst. Cellulose goes into solution at the end of the acetylation reaction. Then this undergoes hydrolysis to get the desired acetyl value of cellulose acetate. Cellulose triacetate is then precipited by using weak acetic acid. It is washed and dried in the customary fashion.

Fibrous Acetylation Process or Heterogeneous Process

The process is just the same as in solution process except that a non solvent for cellulose acetate is included in acetylation bath. This prevents the cellulose ester formed from dissolving in acetic acid so that fibrous cellulose triacetate is obtained.

Kodak first attempted the casting of base on drum casting machine. Bauchet & Co also started casting of base on drum casting in 1926 and switched over to band machines in 1928. Now band machines are being widely used. The problem of casting surface was resolved by the perfection of a technique of highly polished stainless steel bands and are manufactured by 2 or 3 firms in the world. The length of the band used by the photographic firms vary from 28 to 60 metres, the width from 1.3 to 2 metres. HPF also manufactures base on band casting machine.

The process of manufacturing film base consists of the following stages:

Preparation of Collodion

The name collodion has been in vogue since the time of cellulose nitrate base manufacture and the same is being continued for cellulose triacetate solution also. The collodion to be cast as transparent film base is a solution of cellulose triacetate in methylene chloride and methyl alcohol along with plasticizers triphenyl phosphate and dibutyl phthalate. The function of the plasticizer is to impart certain physical and chemical properties to the polymer cellulose triacetate such as toughness, flexibility, tensile strength, gloss, water resistance, fire resistance and electrical properties. Triphenyl phosphate is an excellent compatible plasticizer for cellulose triacetate which imparts the above mentioned properties and also minimises the effect of ultra violet rays on the plastic. Dibutyl phthalate is a co-plasticizer which increases the glossyness of the base. Collodion is prepared in specially designed stainless steel mixers and is processed for obtaining the necessary characteristics. The viscosity of this dope is adjusted to the desired value. The uniform viscosity of the dope is an important criteria for getting the base of uniform thickness. The process dyes required for different products are added and the density checked at this stage. The collodion then undergoes successive stages of filtration to remove all suspended impurities. The filtered collodion is stored in stainless steel tanks in an air-conditioned area. At this stage it is deaerated by vacuum for removing the dissolved air to prevent the formation of air bubbles on the base during casting. Collodion undergoes thixotropic phenomenon a sol-gel transformation during its process of mixing, filtration and storage.

Casting of Collodion

The process is a refined form of uniformly spreading collodion through a "Casting Hopper" on to a continuously moving mirror-polished surface of a stainless steel band across the width in a totally enclosed tunnel. The most important breakthrough technology in the manufacture of base was the design of the casting hopper. The casting hopper is made of stainless steel and the inside of which is so designed as to enable the collodion to flow through a gap between two lips. As the band moves in the tunnel, the solvents evaporate allowing the solids to set in the form of a flat sheet/base. The semi dried base is continuously stripped off the band when it completes one revolution before the casting hopper and the band moves on to receive fresh collodion coming out of the casting hopper. The stripped base is dried in a festoon type of dryer and the base is wound on special mandrels. This film is a continuous sheet from the casting point to the winding end. The solvents evaporated in the basecasting machine is recovered by an Ammonia Refrigeration System and reused for the process.

Of the many physical, optical and chemical properties the base is required to possess, like surface quality, tensile strength, elongation, fold resistance etc. The thickness of the base is also an important criteria. There are special devices in the basecasting machines to control the base thickness. The thickness of the base for different products is different. For amateur roll film, the base must be flexible enough to permit winding on a small diameter spool and as such the thickness of base is 0.1 mm. The motion picture requires a stronger, tougher base with better wearing qualities since it has to be run on projectors many times. So the thickness of the cinema films is 0.14 mm. X-ray films and sheet films for portrait or commercial use should be flat under all atmospheric conditions. For this reason, the thickness of the base for these purposes is 0 2 mm. Incidentally, HPF has developed the technique of making very thin base of 0.025 mm to a very thick base of 0.4 mm for applications other than photographic films. The technical data sheet of cellulose triacetate foils showing physical, chemical, thermal and electrical properties is appended herewith. Cellulose Triacetate base has been found suitable in various applications like insulation materials in Electrical Industries, power cable wrappers, insulation tape industry, packaging industry for lamination purposes, bangle industries, manufacture of goggles and in telephone industries.

HPF started production of films in 1967 by imported Cellulose Triacetate from France made by homogenous process. Later M/s Mysore Acetate and Chemicals, Mandya started supplying heterogeneous cellulose triacetate in 1970. The design of the solvent vapour circuit in the base casting machines had to be modified in 1971 to suit the indigenous raw materials to obtain the desired physical properties of the base. The indigenous cellulose triacetate is slightly different in some characteristics to that imported Cellulose Triacetate by virtue of its method of manufacture. HPF had some problems due to this and it was overcome by modification of the machines. HPF doubled the capacity of base production in 1974 over the installed capacity and this was possible entirely due to technical know how of the HPF staff without any external assistance. Now Filmbase Department has extra casting capacity which can be utilised for the diversification of its products other than photographic films.

Development Work

There is further scope for increasing base production by gel-casting process using a third solvent as per the literature.

Here a mixed solvent containing a poor solvent such as benzene, Tolune or cyclohexane has to be used along with Methylene Chloride and Methyl Alcohol for making Cellulose Triacetate solution. This has the advantage of early coagulation and stripping of base in the base casting machines and thereby improving the speed of casting. The above mixture of solvents has an effect on improving mechanical strength of the dried film. So this process is particularly suitable for making superior quality base.

Substrating Process

The spools of raw base turned out from the base casting machines require a further treatment known as substrating before being sent to coating section. The film base surface is non polar in character. The photographic emulsion on the other hand is an aquous solution. The subbing process is carried out by etching the surface of the base, to ensure adherence between hydrophilous photographic emulsion and hydrophobic film base. At this stage, the gel coated base is ready for coating photographic emulsion on base.

Preparation of Photographic Emulsion

The emulsion is a light sensitive material coated on the base. The nature of processing and the degree of control employed in the preparation of emulsion determine the properties such as light sensitivity, fog, contrast and spectral sensitivity. The principal materials used in the preparation of emulsion are silver nitrate, alkali halides and gelatine. Many special chemical compounds are also used in the preparation of emulsion. The main aim in emulsion technology is to attain the best image quality and least fog. The emulsion manufacture is indeed unique among chemical processes.

Coating of Emulsion on the base

The base is coated in total darkness or in safe light. Coating machines are automatic and are controlled from panels with remote indicating, recording and controlling instruments installed in a separate lighted area. A specific concentration of silver halide expressed as silver per unit area of the base must be obtained in the coated layer. The coating machines consist of coating, drying and winding sections. The base is unwound at one end and it runs through the emulsion trough where the surface of the base picks up emulsion. The coated base enters a low temperature zone for chilling the emulsion layer to form a gel which is held firmly on to the base. The coated base is dried in drying chambers under definite conditions of temperature and humidity. Static electricity charges are generated at all times and is caused by sudden separation of two bodies in contact i.e., the film leaving the roller. When the charges accumulate it does enormus harm to the coated base by way of fog when the discharge takes place. Dust and dirt are easily attracted. Those are avoided by suitable arrangements in coating machines. The emulsion coating should be uniform in thickness. There must be no dark or light spots, longitudinal and transverse stripes, repellancy spot, bubbles and foam etc. The coating density should be constant and the emulsion layer must be free from dirt. Coating of emulsion on base is done on two types of machines namely tunnel dryer and festoon dryer.

Conversion

The coated base after curing is sent for Converting operation in safe lights under rigid control of temperature and humidity. The X-ray and Photographic papers are cut into sheets of different sizes in slitting and cross cutting machines. The cine positive, cine sound film jumbos are slit into 35 mm and 16 mm rolls of 600 mts length and perforated on both sides for 35 mm and one side for 16 mm in perforating machines. The roll films are slit, cross cut, spooled and wrapped in automatic machines. The finished goods are suitably packed for despatch.

Quality Control

Stringent quality control methods are employed at every stage of photo film production to ensure high quality products are supplied to the customers/consumers. For this purpose HPF is using sophisticated instruments like X-ray Defractometer for monitoring the silver weight in the coated material and automatic densitometer for measuring the sensitometric characteristics of the coated film.

Photographic Paper

Papers for photographic purposes are made from highly purified wood cellulose fibres to ensure maximum permanance both in color and physical properties. They must be free from foreign substances and other impurities which would otherwise affect the emulsion. It should have good wet and dry strength to withstand the process. Various thickness from 0.12 to 0.25 mm are made in different grades of paper. The properties that are important are stiffness, tensile strength, dimension stability, crease resistance, curl and bursting strength. Chemical determination will include moisture, ash content, sizing materials, acidity, glycerol, reducible sulphur and other impurities. For photographic papers barium sulphate coated paper is used as base. The coating consists of barium sulphate dispersed in gelatine provides a pure white reflection and good adhension of emulsion. For a high glossy surface a heavy application of baryta upto 40–50 gms/sq.m is given in more than one coating. The effect is further enhanced by calendering process. Depending on the thicknesss of the paper the classifications are light weight, single weight, medium weight and double weight. The thinnest of light weight grade is used for instrument recording work, document copying and engineering drawing. The surface of the paper is described in such classifications as "Texture and Brilliance". Texture covers the smothness of the sheet and ranges from smooth, fine grained, silky rough. Brilliance describes the sheen of the print and varies from 'glossy to lustre'. Paper being essentially a mat of cellulose fibre it is readily capable of taking or losing moisture from the air. In order to eliminate these defects efforts have been made by the manufacturers to give special coatings. Four different types of emulsion are coated on paper namely soft, special normal and hard grade emulsion. Finally emulsion coated and dried papers are cut into different sizes and packed. At present the Baryta coated paper base is being imported to the tune of nearly 6 million sq. mts., since this quality of paper is not being manufactured in India. The annual consumption of paper base in India is in the order of about 1200 tonnes and it is anticipated to increase in next few years. It would be in the National interest to undertake manufacture of this quality of paper for the requirement of photographic industries in India.

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Cellulose Triacetate Foil—Technical Data Sheet

(Not a Specification)

Cellulose triacetate foil is a high grade, heat resistant electrical insulating foil available in a wide variety of thicknesses ranging from 0.04 mm to 0.40 mm. It has low water absorption and good dielectric properties. Its high thermal stability and low shrinkage at higher temperatures make it especially suitable for high-temperature applications (continuous exposure to 120°C, short term exposure to 150°C) where a certain amount of stiffness is desired. It is flame resistant i.e , it ceases to burn within a short while after being ignited.

Cellulose triacetate foil is resistant to mineral oils (transformer oils) and aliphatic hydrocarbons. Aromatic Hydrocarbons and alcohols cause some swelling but this disappears after removal of the solvent. Esters, acetone and chlorinated hydrocarbons (particularly Methylene Chloride) being solvents and strong swelling agents for CTA, should not be brought into contact with it.

1. Chemical Properties		
1.1	Moisture absorption after 1 hr. immersion %	1.0
1.2	Hygroscopic co-efficient of expansion in/in/% RH	6×10^{-5}
1.3	Fungus resistance	inert
1.4	pH value of water extract	6.9
2. Physical Properties		
2.1	Tensile strength Kg/mm²	8.5
2.2	Modulus of elasticity Kg/mm²	310
2.3	Elongation at break %	20-25
2.4	Fold endurance	10
2.5	Specific gravity	1.28
2.6	Refractive Index	1.48
3. Thermal Properties		
3.1	Heat distortion temperature °C	150
3.2	Permanent heat resistance °C	120
3.3	Melting Point °C	...
3.4	Co-efficient of Thermal expansion 10^{-5} in/in/°C	3.0
3.5	Shrinkage (ageing 1 year at 25°C, 60% RH) %	0.15
3.6	Softening Point °C	150
3.7	Shrinkage % after 24 hrs. at 150°C and 65% RH	6-7
4. Electrical Properties		
4.1	Breakdown field strength after 24 hrs. in air at 20 ± 2°C and 80% RH Sample thickness 0.200 mm	50Kv/mm
4.2	Dielectrical strength volts/mil	1250
4.3	Insulation resistance after 24 hrs. in air at 20 ± 2°C and 80% RH/cm³	10^{13} ohms
4.4	Surface resistance after 24 hrs. in air at 20 ± 2°C and 80% RH/cm²	10^{14} ohms