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5.5 Plastic Materials

Paolo Carollo, Barbara Grospietro*

Acetati S.P.A Viale Azari ,110, 28922 Verbania (VB), Italy

Summary: The History of plastic CA and evolution of its markets is summarized with reference to applications. The main products (diacetate granules, and sheets) and technologies are described in terms of characteristics and flowchart. A special focus is dedicated to Diacetate sheets technologies (block process, extrusion process).

Keywords: Diacetate Granules, Diacetate sheets, Block process, Extrusion, Compression sheets.

5.5 Plastic Materials

5.5.1 History of plastic CA and evolution of its markets

The earliest applications of plastic acetate date back to 1910 when the Dreyfus brothers produced the first photographic film from acetate. The development of other applications soon followed, fulfilling the need to find a substitute for celluloid, which was too flammable to be used in large-scale production or with high speed pressing process.

Cellulose acetate was initially produced in bars, sheets, and tubes, the same forms as celluloid had been, but in 1927 a moulding powder/compound became available which could be transformed quickly and cheaply through injection moulding.

In the meantime diacetate was becoming a popular substitute, as celluloid had been earlier, for natural materials which could no longer be employed because of decreasing availability and increasing cost (animal horns), as well as risk factors (the high inflammability of celluloid) and environmental restrictions. Inventive and multiple uses and applications were found immediately for the new material: eyewear (1922 France), fashion accessories, costume jewellery, combs, buttons, packaging, plastic handles for sanitary equipment, pens, utensils, toys, and technical items. The diffusion of the numerous applications of acetate reached its peak in the 1960's: boxes and blisters were manufactured through the process of extrusion blow moulding, and destined mainly for food packaging, while windshields, lampshades, shatterproof crystals for watches, accessories for the automobile industry and safety glass constituted the wide variety of goods

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being produced for this growing market.

Today many of the specific applications in vogue in the '60's are no longer in use or popular, but diacetate is still the material of choice in the manufacture of many plastic products whose use implies direct and prolonged contact with humans.

5.5.2 Applications

a) Fashion and accessories

Of all the thermoplastic materials available, cellulose diacetate is the only one able to satisfy the requirements of applications which demand the co-existence of sensorial qualities (touch / visual appeal, comfort), hygienic-health qualities (hypoallergenic, tolerable to prolonged physical contact), and environmentally friendly (biodegradability and low flammability in comparison to other cellulose derivatives).

As well as its transparency and colour fastness and brightness, the typical deep and warm chromaticity is able to give the impression of worth and has its source in nature and its gradations, nuances and shades.

Its transparency is not vitreous or glasslike but can assume aspects which generate the desire to wear colour or hold a familiar object.

The ease of coloration and the satisfactory chromatic results also facilitate the manufacturing process, and have encouraged the use of acetate in all of the fields where colour plays an important roll. It has thus become a constant element in our daily lives, both at work and at play: eyewear, costume jewellery, buttons, accessories, decorative sequins...in all of its applications diacetate interprets both creativity and style.

Various manufacturing techniques can be used in such a way that acetate's chromatic value can be fully exploited. The colour of the acetate is married to whatever design the particular process is capable to produce. A tri-dimensional design, thanks to the transparency of the acetate, highlights the diffusion and the diffraction of light and thus renders the chromaticity of the finished product unique in the world of fashion accessories.

With the processing know-how developed over the last few decades, starting with the invention of polymers up to today's more recent innovations, there exists a practically infinite series of effects which can be obtained through both the profundity and the complexity of the designs, as well as through alternating colour effects and nuances that can range from transparency through to imitation opal, Chinese lacquer and mother of pearl.

Natural materials are combined with polymer in a technology where man's expertise and creativity play an important role.

Cotton and wood pulp are thus transformed into manufactured items and fashion accessories according to the perfect rules and colours of nature.

Natural effects such as tortoiseshell, horn and mother of pearl obtainable from diacetate have characterized the way we look and made fashion statements since the 1950's. In the world of fashion the most famous designers have all used acetate to decorate their creative designs. In doing so they have promoted the use of this natural and natural-looking material with its vast chromatic range.

With its flexible technology, fashion trends can be readily followed. Just as new fabric and finishing details are developed, so too can the colours and structural features of acetate be adapted to the variety of demands and requests of designers and the seasons.

b) Visors / protection

The high quality of the material and its perfect transparency have led to its use in two other important markets: athletic and safety equipment.

Ski masks boasting the most prestigious brands are mainly produced with cellulose diacetate.

Not only can the polymer be tinted so as to guarantee protection of the wearer's eyes from the snow's glare, but by adding special additives it can also protect up to 400 nm of the sun's rays.

Correctly-treated diacetate is able to answer another important request of those who practice winter sports as well as those using safety devices: the necessity of antifog treatment. Diacetate is the only polymer that can be rendered antifog so effectively. A recently developed application can also produce photochromatic sheets which facilitate the passage from sunny areas to shade.

In the sports market, along with ski masks, mention must be made of swimming goggles which, because of their use in wet environments, must be also feature high quality antifog properties.

And finally, another significant market for acetate is that of safety devices which can guarantee both transparency as well as protection from IR rays.

c) Brushes and handles

Transparency, smoothness and colour have also played important roles in the use of this material for applications connected with health and hygiene (toothbrushes), fashion (umbrella and handbag handles) and manual work (screwdriver handles).
Not an accessory but an important practical application of acetate who has never held an orange, green or red-handled screwdriver or admired a brightly coloured series of tools in a garage, a factory or a do-it-yourself home workshop or tool box. Colours that liven a up the usually rather drab atmosphere of manual labour and render these tool touch and user friendly and comfortable.

d) Packaging

Producers of expensive and prestigious shirt still deliver their products in bright shiny boxes manufactured from acetate film.
Other materials could be proposed but an item that is so personal has to convince right from the first contact with the cover of the box which in this case, is just as smooth and pleasing to the touch as the cotton fabric of the shirt contained within.

e) Casino games

Thanks to the above-mentioned qualities diacetate also makes its mark in gaming rooms in the form of casino chips and playing cards. They add to that intriguing atmosphere of colour, carefree pleasures and hopefully, luck. Continuous contact with the skin, the ease with which they slide across the table, the noise the chips make as they click against each other in player's nervous hands, the colours, are all an integral part of the furnishings and conducive to that particular hush and magic that permeates the ambience.

5.5.3 Products and technologies

Thanks to its specific characteristics of strength, resistance and versatility of colour, cellulose acetate is largely processed using injection and extrusion moulding and casting.
Cellulose acetate needs plasticizers and additives in order to undergo the various manufacturing procedures. The plasticizers (which can vary in number and in proportion, from 10 to 70 per cento of the acetate) are normally liquids with high boiling points and low vapour pressure and

characterized, in any case, by a high affinity with cellulose acetate.

By varying the characteristics of the cellulose acetate (in particular the percentage of acetic acid and the average grade of polymerisation), choosing the typology and quantity of plasticizers, adding colorants, UV absorbers, stabilizers, bleaches, optic agents, opacitors, brightening agents, inhibitors, metallic dust /powders etc., the plastic that results can vary enormously and the creative possibilities are practically unlimited.

5.5.3.1 Characteristics and Types

Commercial cellulose diacetate exists in white powder or flakes with a humidity content of less than 1% and a bulk density between 200 and 500 g/lt.

The basic typologies can be differentiated according to their acetic acid content and to the application they are destined for. Other typologies can then be derived from these and used for special and more specific purposes.

Acetates with about 56% combined acetic acid are normally used for the production of moulds using the blow moulding process,

Acetates with 55% combined acetic acid are normally used in injection moulding and casting,

Acetates with 54% combined acetic acid are normally used for the extrusion of film because of their particular affinity with plasticizers,

Acetates with 53% combined acetic acid are used for the production of sheets using the "block" process.

Cellulose acetate and the manufactured articles that result are odourless, tasteless and non-toxic; they are not subject to electrostatic charges, have good resistance to oils and solvents and are excellent electric insulators.

Applications and markets obtained from acetate presented thus far can be summarized as follows:

Table 5.5.1 Products and applications of plastic diacetate

Product	Applications
(a) GRANULES	Screwdriver handles, brushes, injected-moulded articles for costume jewellery and hair ornaments, sheets for eyeglasses and safety goggles
(b) FILM	Packaging, adhesive tape and magic tape, shoelaces, sequins 0,5 mm thickness.
(c) SHEETS	Eyewear + costume jewellery + hair ornaments (handcrafted); athletic and safety visors, casino chips, buttons, handbags and handles 0,8 – 10 mm thickness.

Different production technologies correspond to the three main final products (granules, film and sheets) but all of the processes have the initial mixing phase in common.

The mixture of cellulose acetate with other components can be carried out without solvents, using heated rolling mills-laminators, with extrusors and mixers that can be set at either slow or fast speeds and at temperatures ranging from 120 to 220° C.

5.5.3.2 Diacetate Granules

Cellulose Diacetate is hygroscopic and for this reason granules must be dehumidified through proper hot air and dehumidifying systems before being subjected to the injection process. If granules are produced for extrusion the material must be dried in special dryers or extruded by stripping.

The water which results in these conditions is such that it can act as a co-plasticizer.

Diacetate's absorption of humidity affects not only the process (where the material must always first be dried or worked by stripping) but also the stability of the final product. In items having extensive surfaces the absorption of humidity could cause distortion of the surface structure and sufficient dimensional stability cannot be guaranteed.

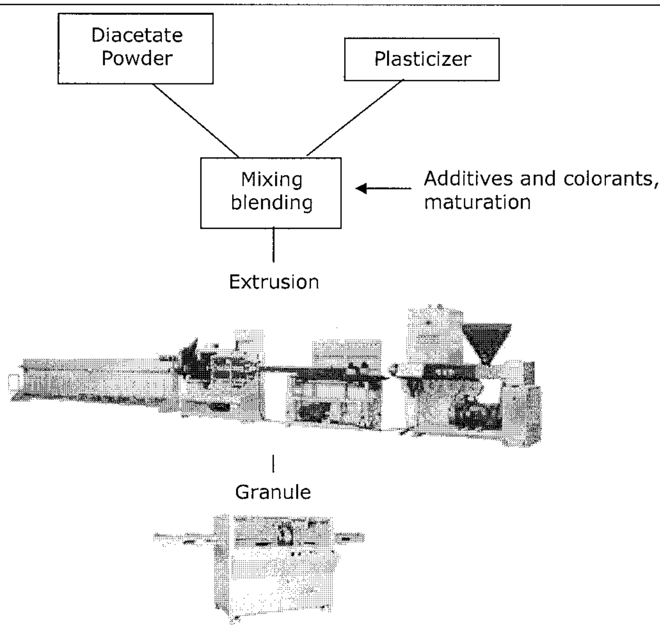
The presence of plasticizers (essentially phtalic esters) and their possible migration or random movement within the acetate requires a certain care and caution in deciding on eventual applications, keeping in mind that they could be exposed to subsequent problems or irregularities. In any case a wide range of plastifying agents exists which can satisfy the various requirements of both the process as well as the users' eventual needs.

Chromatic possibilities are vast and range not only from transparent to opaque, pearlized to opalesce but include fluorescent, bleached, and photo-chromatic effects as well, thus resulting in an extremely versatile material for a great variety of applications which demand particular aesthetic qualities. Injection moulded articles can require additional colouring (for example spraying) and/or dying since the material is generally moulded in single colours (transparent or light shades).

Manufactured items are usually subject to finishing procedures such as buffing and polishing.

Table 5.5.2 Granules production process

Process flowchart



Slow or fast mixers may be used for the amalgamating phase by rotation in various directions and at various speeds. Extrusion calls for the use of both single-screw and double screw extrusors with stripping done through a perforated drum.

Earlier processing used roll mills rather than the extrusion process.

In a typical procedure for the production of granules suitable for injection moulding and for the extrusion of specific shapes and film, consists in mixing cellulose acetate powder with the plasticizer in a dry-blender at room temperature.

The powder is then aged or "matured" at a temperature of 60-80° for a few hours and then sent through the extrusion process after which it is cut in the different forms as needed or requested by the market.

5.5.3.3 Cellulose acetate film

Obtained from granules through extrusion or blow moulding and sold in bobbins of different sizes according to the needs of the markets, acetate film is used for packaging, fashion accessories (sequins) and plastic-tipped shoelaces.

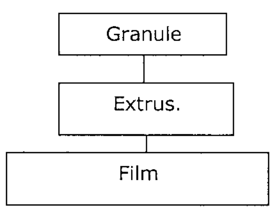
The film produced is usually transparent and is cut to measure, heated and then folded to make boxes or containers.

In the case of sequins, the film is cut into tiny roundels that undergo a particular bleaching process. These are then sewn onto items of clothing and various fashion accessories (small purses and evening bags, etc.).

Among the various uses of film, a bio-degradabile version has become extremely popular for packaging. The micro-organisms in this kind of film provoke an enzymatic hydrolysis of the polymer resulting in the liberation of the acetic acid and the subsequent breakdown of the glycosidic ties. The final step is the destruction of the glycosidic chain and its transformation into methane, carbon dioxide and water.

Table 5.5.3 Film production process

Process flowchart



5.5.3.4 Diacetate sheets

The market for sheets is the one that allows Diacetate to best express its chromatic qualities and tactile values.

Eyewear, costume jewellery, hair ornaments, and buttons all supply fashion's various stylistic needs and proposals: the expertise with which sheet manufacturers can colour or tint the material and the creative capacities of the client who produces costume jewellery and fashion eyewear are at the basis of the success of these polymers, still in great demand even 100 years after being developed. Apart from buttons, all of the other articles obtained from acetate sheets remain in contact with human skin for long periods of time throughout the day and are subject to climatic conditions both indoors and out.

Diacetate is hypoallergenic and mitigates notable contrasts and changes in temperature thus protecting wearers from adverse affects.

High temperatures in summer or in hot climates as well as the rigorous temperatures of winter are absorbed by Diacetate which can carry out its function as an accessory without the user having to put up with the discomfort extraneous items often cause (a phenomenon on the other hand typical of many technological materials and metals in general).

Over 70% of the sheets destined for eyewear, costume jewellery and hair ornaments are multicoloured.

A combination of colours can be obtained thanks to sophisticated technologies (which will be explained in the following pages) developed in recent decades; from the earliest, which produced the composition of the material using methodologies based on the manual skills of operators to more advanced techniques which employ sophisticated systems of mixing colour with material in a state of flux.

Imagine watching an artist in his studio as he manually composes a work of art with coloured materials, or a weaver who can produce textiles rich in pattern and colour on a loom.

With this process it is possible to reproduce perfect imitations of tortoiseshell and horn, natural materials, with which eyeglasses, hair ornaments or combs and buttons, can be obtained. Subtle effects of shading, which can light up or soften a face, colourful patterns, like a black and white checkerboard design, or opaline stripes, bleached, fluorescent, dark nuances, as well as printed silk-screen designs can all be created.

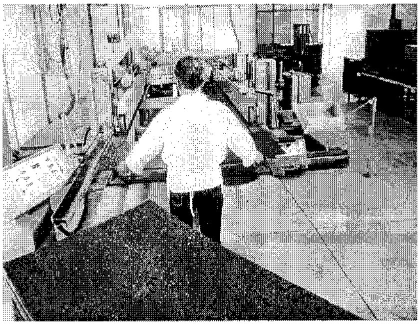


Fig.1: part of sheets production process

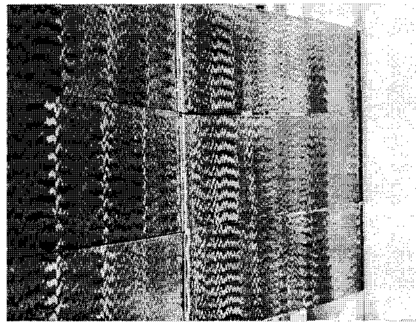


Fig.2: sheets ready to be used for end products manufacturing

With the vast range of colour combinations available, once the sheets have been heat processed, they can be moulded, fashioned and finished as desired.

The product will be the fruit of a long creative process begun from the moment the sheets are prepared for elaboration and ending with the finished pair of eyeglasses, bracelet, earrings, hair clip or button. The working and finishing techniques used depend on the purpose and destination of the object. For costume jewellery or hair ornaments the sheets are cut being previously heated and resulting in a semi-finished product which will then be submitted to further finishing processes.

Mechanical cold-working with routers, or fraising (pantography) are also possible and pieces of diacetate can easily be glued together using a diacetate and acetone-based glue.

For eyewear, two main kinds of processes are used:

- Frame front: The sheets (5 – 8 mm) are cut into rectangular shapes of circa 160 x 70 mm

They are then pantographed to obtain the internal grooves (where the lens are inserted) and the external profile. Thus little remains of the original rectangle (only about 10-15%). Further processing transforms the section obtained giving it its definitive form.

Cellulose acetate can also be easily submitted to buffing processes to attach hinges and decorative metallic ornament.

The formation of the nosepiece is done through heat processing (with the plate heated to H.F.).

- Earpiece: Sheets of 3,5-4,0 mm thickness are cut (cold or hot-worked) into rectangles into which the metallic elements are heat injected.

The rectangle is generally worked and shaped according to the stylistic needs determined by the front-piece of the frame.

All of the products obtained must then be polished using a rather complicated-complex bolting procedure that requires various phases of buffing and polishing.

The sheen or gloss of the material is a typical characteristic of diacetate and distinguishes it from all the other polymers.

Its high gloss and quality of colour, and its tactile comfort are due to the chemical/physical characteristics of the polymer and its formulation.

Today there is no substitute for diacetate sheets in the manufacture of costume jewellery and eyewear thanks to its properties of transparency, the vast range of colouring possibilities, gloss, ease in cutting, mechanical processing and gluing, tactile compatibility, and being hypoallergenic, light fast and resistant to atmospheric conditions and pollution, as well as its use in processes that favour complex structures and colours. All of these are features of this material that do not exist in any other polymers. Today the use of sheets in the manufacturing of buttons is strictly limited to high quality, high cost designer fashions.

The sheet sector supplies two other important markets: athletic and safety equipment. In sports the optical qualities of acetate sheet is especially appreciated (thanks also to the sophisticated polishing processes that can be adopted) because of the ease with which the material can be coloured and its anti-fog properties.

Thin sheets are punched into protective visors, ski masks and swimming goggles.

The limitations of the acetate mask lie in its limited resistance to scratching which expose diacetate to competition with more technical polymers such as polycarbonate. However this material's anti-fog qualities are inferior to diacetate's.

The manufacture of casino chips from sheet acetate is limited to certain structures and characteristic colours. The different chips are cut and coloured and then each monetary value is imprinted in gold.

The processes used for obtaining sheets are essentially the following:

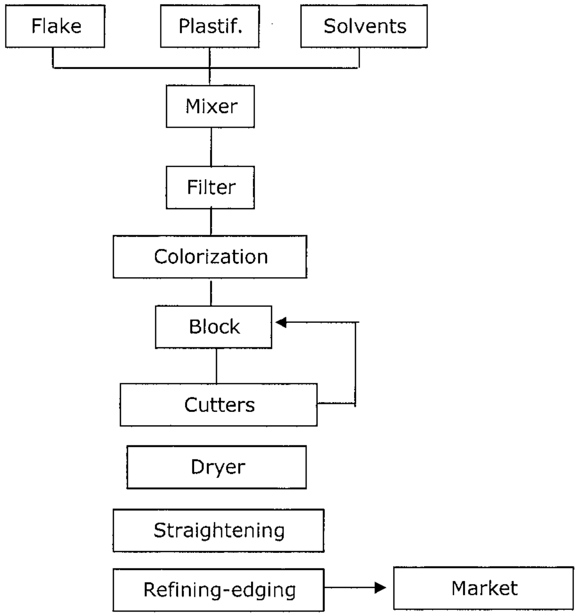
A. Block
B. Extrusion
C. Compression

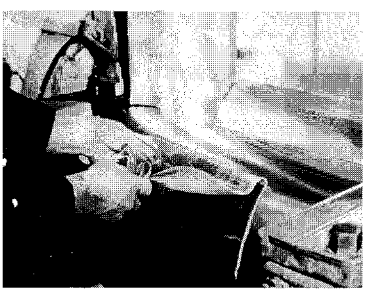
A. Block

The Block process represents the oldest technology and can be diagrammed as follow:

Table 5.5.4 Film production process

Process flowchart





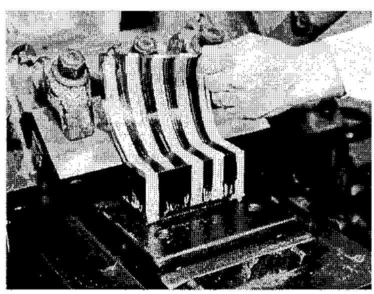


Fig. 3, 4 phases of block production process

Today only two plants in the world produce acetate sheet using this technology: the process is extremely long (it takes about 6 weeks to complete), and involves a high level of skilled manual workmanship; in its favour is exclusivity of design and special chromatic effects.
Plasticizers and solvents are added to the flakes, and the composition is blended in a slow mixer until a soft paste is obtained which must then be filtered to eliminate any impurities. Colouring agents are then added to the filtered paste using double cylinder mixing drums?
At this point a soft sheet, generally a single colour, results which is then placed in a press to obtain a block measuring 700x1400x300 mm. The block is cut into sheets of varying thickness according to need. The processes used can be articulated in the following phases:

1. If a single colour sheet is desired the soft sheet (still rich with solvents) is kiln-dried for about 10/20 days depending on the eventual thickness required.

2. Single-colour sheets produced in the first phase are then manually re-composed in the presses, following precise procedures, to obtain a design of multiple components. The multicolour block is pressed and then re-cut. This cutting and re-composition process can be repeated 3-4 times to realize designs otherwise unobtainable using other techniques.
After the final cutting the sheets are dried.
The drying process and the pressing period allow, thanks to factors such as time, temperature and pressure, particularly subtle effects of shading to be obtained. This is due to the presence of migrating colours exclusive to this technology and unique to the procedures used in the working of plastic materials.

3. Each sheet is then placed in a multi-story press so that the surface, which tends to come out of the kiln wavy or irregular can be straightened and rendered smooth.

4. The edges of the sheet are squared and it is trimmed down to its final size (usually 600x1600). After this last step the sheet is ready for shipping.

The block process can add an aesthetic advantage to the intrinsic values of acetate (ease of coloration, tactilely pleasing, ease of working and polishing, light fastness and resistance to atmospheric agents). The solubility of diacetate in environmental and user-friendly solvents is

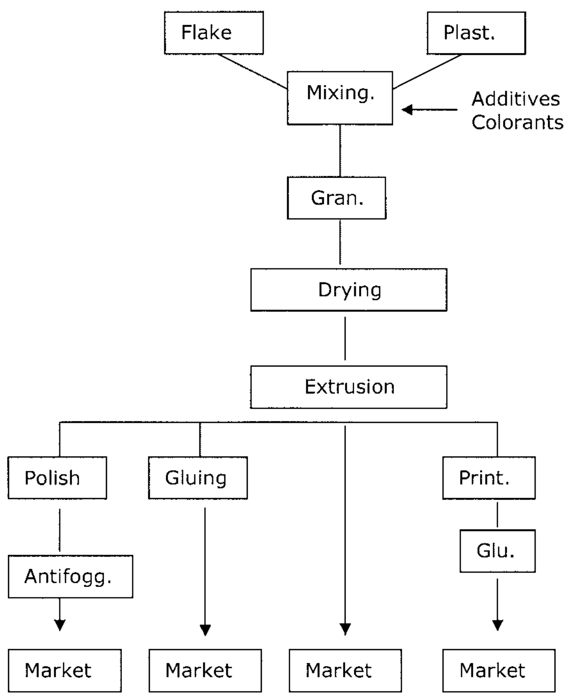
also unique and no other material today can be utilized in similar process.
However, due to diacetate's lack of dimensional stability, these aesthetic and sensorial values cannot be taken advantage of in more markets.

B. The extrusion process

This process was developed towards the end of the 1960's as an alternative to the block process which was so slow and time-consuming.
As extrusion is a continuous process, running time takes only a few hours. With service logistics and considerations increasingly more critical this technology signified an important development.
The process can be summarized in the following diagram:

Table 5.5.5 Film production process

Process flowchart



For sheet extrusion the granules must be dried or extruded by stripping.

Most of the sheets used in the production of eyewear are produced by multicolour plant facilities in the sense that more colours (up to five) are co-extruded in a single spinneret-threader.

The designs obtained are generally less sophisticated than those created with the block process since they are realized with mechanical equipment which prints material in flux: thus designs are generally single direction (one-way) obtained through extrusion or overlapping structures, consisting of as many layers as there are colours. The advantages of this process, as mentioned before, are tied to reduced delivery times (since the sheets do not require final drying) while its limits lie in obtaining less sophisticated designs as well as to the number of lots that can be produced since economical factors are affected by start-up times and colour changes in a continuously running plant.

In the block technology on the other hand, the process is not continuous, there are no scraps from start-up or colour changes and the quantities that can be produced are only tied to the complexity of the designs and the capacity of the press.

The extruded sheets can then be screen printed and then eventually glued to other sheets to obtain more sophisticated effects.

Although other transparent materials could be extruded to obtain similar effects they cannot be worked or processed (cut, milled, glued, and polished) as easily as acetate. Thus limits are imposed only by those characteristics of the product dictated by the market and become a "must" rather than by the extrusion technology itself.

For safety visors, the extruded sheets are optically polished and then an anti-fog treatment is applied.

C. Compression Sheets

This technology was developed towards the end of the 1980's in order to obtain effects similar to those produced in block technology but without being constricted by the considerable lengths of time needed to prepare the sheets.

The main objective was to recreate subtly shaded designs like those imitating tortoiseshell.

The process calls for either the fusion of pieces of plastic material (granules or fragments) or designs and patterns moulded under particular conditions of pressure and temperature. The sheets thus obtained could then subjected to a procedure of accelerated pigment migration which give results like those subtle effects produced in the block process.

The strict processing conditions, temperature and pressure have restricted the use of this technology which in fact is by far the least important of the processes mentioned.

In the following table are summarized some important characteristics of Cellulose Acetate sheets for optical purposes.

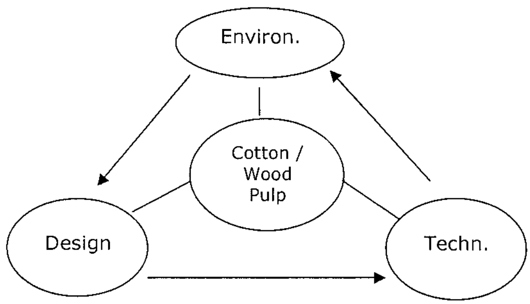
Table 5.5.6 Cellulose Acetate sheets Characteristics

CHARACTERISTICS	REF.		UNITS	VALUES
Physical				
Density	ASTM D 792		gr/cm3	1,28 - 1,32
Refractive index	ASTM D 542			1,49 - 1,50
Water absorption	ASTM D 570	24h, 3,2 mm	%	2,0 - 2,5
Weight loss	ASTM D 570	24h, 3,2 mm	%	0,3 - 0,6
Dimensional stability	ASTM D 1204		%	< 2
Mechanical				
Tensile strength at break	ASTM D 638		Mpa	28 - 34
Elongation at break	ASTMD 638		%	20 - 35
Flexural modulus	ASTM D 790		Mpa	1300 - 2000
Izod impact resistance	ASTM D 256 ISO 180	notched	KJ/m2	4 - 12
Charpy impact resistance	ISO 179	unnotched	KJ/m2	50 - 150
Rockwell hardness	ASTM D 785	R Scale	-	75 - 100
Thermal				
Vicat temperature	ASTM D 1525B	oil Kg 1	°C	90 - 100
Conductivity	ASTM C 177		W -m K	0,2 - 0,3
Coefficient of thermal expansion	ASTM D 696	linear	10 -5 K	10 - 15
Combustion velocity	ASTM D 635	3 mm thickn.	mm/sec	0,1 - 0,2
Electrical				
Resistivity	ASTM D 257		Ohm-cm	10
Dielectric strength	ASTM D 149		KV/mm	10 - 12

The above values are medium values and refer to material conditioned at 23 °C and 50% r.h.

5.5.4 Advantages of plastic CA

Buying acetate means participating in a harmonious cycle that unites man, technology and the environment and the presence of natural elements, whose components allow technology to address man's creativity, continues.



Thus acetate links environment and nature with man's aesthetic, creativity and technological expertise. Each of these elements has a specific role in protecting and perpetuating those economic, historical, social and cultural values developed over the last 100 years.