PHILIPS TECHNICAL REVIEW

VOLUME 40, 1982, No. 10

Manufacture of LaserVision video discs by a photopolymerization process

H. C. Haverkorn van Rijsewijk, P. E. J. Legierse and G. E. Thomas

After its introduction in the United States, towards the end of 1978, the Philips LaserVision system is now on the market in Europe. The players are mass produced in the Philips factory at Hasselt, Belgium, and video discs are made in the Mullard LaserVision Disc Centre at Blackburn, England. The disc manufacture at Blackburn is based on an entirely new process: the information is transferred by curing a liquid polymerizable lacquer on the mould or 'stamper' with ultraviolet light rather than by using the classical method of impressing into a plastic. In 1974 an investigation was started at Philips Research Labortories into the possibilities of applying this process to the manufacture of video discs. After the first fully playable disc had been made in this way in 1976, a team including a large number of colleagues from various product divisions investigated the prospects for mass production. The outcome of this intensive cooperation was the start of pilot production in 1980. After successful completion of the acceptance tests, full production started in 1981 at Blackburn. The European introduction of the LaserVision system seemed to us an appropriate occasion for including two articles on the new process. In the first article the process is compared with other methods and it is explained how it is used in current manufacture. The second article deals in some detail with the investigation of photopolymerizable lacquers for LaserVision discs.

Ir H. C. Haverkorn van Rijsewijk is with the Philips Audio Division, Eindhoven; P. E. J. Legierse is with the Philips Plastics and Metalware Factories (PMF), Eindhoven; Dr G. E. Thomas is with Philips Research Laboratories, Eindhoven.

Introduction

The 'video disc' in the Philips LaserVision system is the size of an audio long-play record. Picture and sound information is recorded on it as a succession of small pits of variable length and repetition frequency. The information is read out optically by the player, so that the read-out system does not come into direct contact with the disc. The operation of the player and the system, and the possible applications, have been dealt with by many Philips authors, both in this journal [1] and elsewhere [2].

Not much has yet been published, however, on the manufacture of video discs. This is because until recently they were produced with the pressing techniques used in the manufacture of audio long-play records. The video discs introduced in the United States were also made with these techniques. The information on these discs is recorded to suit the NTSC colour transmission system, which makes them unsuitable for use in the European countries where the PAL system is used [3]. For the production of video discs in Europe Philips are employing a new method, based on a photopolymerization process known as the '2p process' (from *p*hoto*p*olymerization). In this process a liquid polymerizable lacquer is cured on an information-carrying mould (sometimes called a 'stamper') by exposure to ultraviolet light.

The first ideas on this application of the 2p process, and actual trials, came from the Philips Research Laboratories in Eindhoven. As often happens, the introduction of an entirely new technology into mass production posed a number of unforeseen problems. Solving the problems that arose on the introduction of the 2p process required the professional skills of many people from several Philips product divisions and the Research Laboratories. The combined effort of this team led first to a successful period of pilot production, followed by the introduction of the process in the production of PAL video discs for the European market, now carried on at Blackburn.

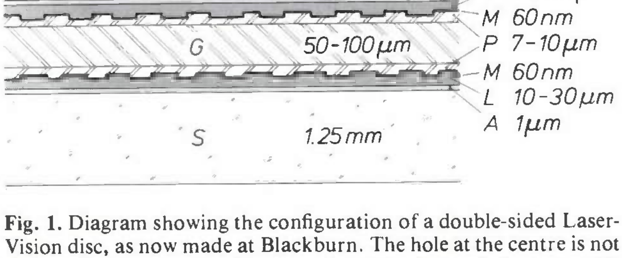


Fig. 1. Diagram showing the configuration of a double-sided LaserVision disc, as now made at Blackburn. The hole at the centre is not shown. *S* transparent substrate. *A* primer layer. *L* lacquer with picture and sound information in the form of pits. *M* mirror coating. *P* protective layer. *G* adhesive layer.

In this article we shall first give a brief description of the LaserVision system in its current form. We shall then examine the manufacture of the discs, considering the reproduction methods in general and the 2p process in particular. We shall then deal with some of the requirements that the video disc has to meet, and with the consequences for the choice of the materials and process control. Finally we shall describe the various materials and the stages in the present production process, indicating some alternatives that are under consideration.

The Philips LaserVision system

The LaserVision disc now being produced at Blackburn consists of two halves, with an external diameter of 300 mm and a central hole of diameter 35 mm, bonded 'back-to-back' with an adhesive. The two disc halves consist of a transparent substrate coated on one side with a primer layer and a lacquer layer in which the picture and sound information is recorded; see *fig. 1*. Since the information is read from the disc in a reflection process, a thin highly reflective metal 'mirror' is applied to this 'information' layer. This in turn is coated with a protective layer to prevent chemical and mechanical damage, which might occur during later stages in the manufacture. The protective layer also serves as a base for the adhesive that bonds the two discs together to form the complete video disc. The information is recorded between the radii of 55 and 145 mm, as a spiral track of small pits 0.12 µm deep and 0.4 µm wide; see *fig. 2*. The length of the pits and the minimum distance between them vary between about 0.5 and 2.0 µm, and the pitch of the spiral is 1.6 µm to 2.0 µm.

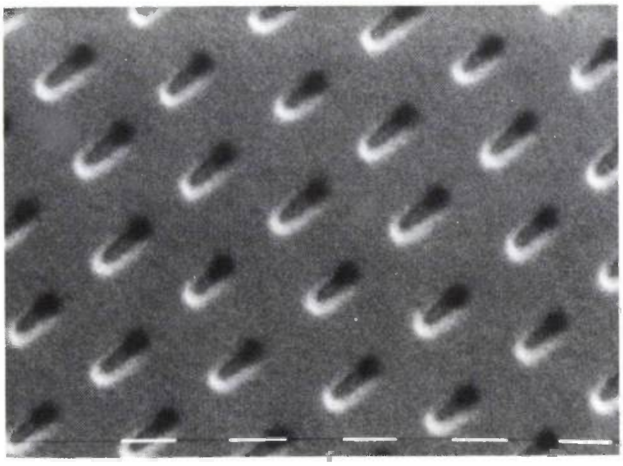


Fig. 2. Scanning-electron microscope (SEM) picture of part of a LaserVision video disc; the dashes correspond to a length of 1 µm. The information track consists of small pits of constant width and depth, with variable length and spacing.

The information is read optically with monochromatic light at a wavelength of 632.8 nm from a helium-neon laser [4]. A moveable lens guided by a control mechanism [5] keeps the laser light focused through the substrate on to the reflecting surface carrying the information. The intensity of the reflected light is modulated by the pattern of pits. The reflected beam is intercepted by a light-sensitive diode that converts the intensity variations into electrical signals [6]; see *fig. 3*. These in turn are translated electronically into picture and sound signals appropriate to a standard television receiver [7].

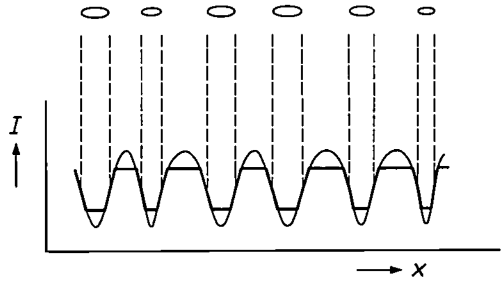


Fig. 3. Diagram showing the relation between the pattern of pits and the LaserVision signal on read-out. The laser light, modulated by the pits, produces a current I in the photodiode of the player. This current depends on the position x along the information track. The trapezoidal waveform is produced by symmetrical amplitude limiting.

Read-out in the LaserVision system can take place at constant angular velocity or at constant linear velocity. In the first case the disc rotates at a constant speed of 25 rev/s, corresponding to the frame frequency of the European television systems (25 Hz), so that each turn of the spiral track contains exactly one frame. As explained earlier in this journal [5], this makes it possible to 'manipulate' television pictures: by moving at the right moment from one turn to another, stationary, speeded-up, slow-motion and reverse-motion pictures can be obtained. The playing time, determined by the speed of rotation, the pitch of the track and the available area on the disc, is more than half an hour on each side. About twice the playing time can be obtained by reading at constant linear speed from a disc in which the information per turn increases with the radius of the turn. The speed of rotation is then gradually reduced as the disc is read from inside to outside. This method is to be preferred when a long playing time is more important than the ability to manipulate pictures. Both types of disc are currently available in the LaserVision system; the player automatically adapts to either.

Manufacture of LaserVision discs

The manufacture of the video disc begins with a 'master', a glass disc coated with a layer of photoresist. Picture and sound information from a 'master' video tape is written into this layer by means of modulated laser light of peak power about 200 mW, so that it is recorded in the form of a pattern of tiny pits; each side of the disc contains about 25 000 million of these pits. As is usual in the production of gramophone records, a metal copy of the vulnerable master is made by electrochemical methods; this is the 'father' mould. After this negative copy has been detached, the master disc is no longer usable. Further electrochemical copying of the father mould produces the 'mother' moulds, which are positive copies of the master. Copying a mother mould then gives the negative copies that are used as the production mould for mass production. This 'family' process enables many production moulds to be made from a single master disc.

We shall not consider these stages further, but will confine our attention to the following stages, in which the video discs are manufactured from a production mould. We shall now review the methods that can be used for replicating the pattern of pits in the mould.

Reproduction methods

For manufacturing video discs an obvious course was to use the standard method for producing audio long-play records. In this method a preheated plastic blank is placed on the information-carrying mould under a press, the press is then closed and heated to a temperature at which the plastic softens. The plastic is then pressed over the mould under high pressure. The plastic fills up the available spaces and therefore takes up the information contained in the mould. After cooling, the disc is removed from the press. An advantage of this method is that a complete side of the disc, with the correct outside diameter and including the centre hole, is obtained in a single operation. The high pressure and temperature, however, can cause some deformation of the mould, so that local non-circularity of the tracks is introduced. There may also be residual stresses in the plastic, producing undesirable birefringence or a warped disc.

Another familiar method is injection moulding. In this method granulated plastic is melted and injected

---

[1] Philips tech. Rev. 33, 178-193, 1973.

[2] Appl. Optics 17, 1993-2036, 1978.

[3] F. W. de Vrijer, Philips tech. Rev. 27, 33, 1966.

[4] See for example K. Compaan and P. Kramer, Philips tech. Rev. 33, 178, 1973.

[5] P. J. M. Janssen and P. E. Day, Philips tech. Rev. 33, 190, 1973.

[6] G. Bouwhuis and P. Burgstede, Philips tech. Rev. 33, 186, 1973.

[7] W. van den Bussche, A. H. Hoogendijk and J. H. Wessels, Philips tech. Rev. 33, 181, 1973.

into the mould cavity. After cooling of the mould cavity a hard plastic disc is obtained, containing a negative copy of the information in the mould. This method is used, for example, in the mass production of small gramophone records (singles). The advantages and disadvantages are comparable with those of the pressing process.

In view of the special requirements that the video discs have to meet, a number of alternative reproduction methods were investigated, both at Philips and elsewhere [8]. In one of them, called the 'printing method', a heated mould is used to impress the information at high pressure and temperature into the surface of a plastic disc at room temperature. The heating softens the surface of the disc so that it can take up the information contained in the mould; the information is then 'frozen in' by fast cooling. In principle only the surface of the disc is affected in this process. However, since it is difficult to obtain disc blanks that are sufficiently flat, the discs must be preheated so that complete plastic deformation is possible. In addition there are the disadvantages mentioned earlier of high pressure and temperature, and extra operations are necessary for making the centre hole and obtaining the correct outside diameter.

Another method, using the 2p process referred to in the introduction, was found to have many attractive aspects. These led to the introduction of this process for current production.

Application of the 2p process

In the 2p process, monomers of acrylates (esters of acrylic acid) are polymerized by exposure to ultraviolet light [9]. The polymerization is started by the addition of a photo-initiator. *Fig. 4* is a diagram of phases in the 2p process. A few millilitres of the 2p lacquer — one or more monomers with a suitable photo-initiator — are applied to the centre of a mould. A transparent plastic disc, the substrate, which is slightly deformed to make it convex, is placed on the mould. The substrate is then pressed flat again by applying a slight excess pressure, causing the lacquer to flow out from the centre to the outside edge, covering the surface of the mould. The space between the mould and the substrate is thus filled by a thin layer (10-30 μm) of liquid lacquer, so that the information contained in the mould is completely transferred to the lacquer. The lacquer is then exposed to ultraviolet light at a wavelength of about 350 nm through the substrate, causing the lacquer to polymerize and become hard. The composition of the 2p lacquer is selected such that it does not adhere to the mould after curing but does adhere to the substrate; a primer layer may be used if necessary [9]. After the exposure, the video disc — the substrate with the cured lacquer — is removed from the mould. The mould can be used again immediately for making the next disc.

This process can be used with substrates that already have a centre hole. Further mechanical operations are necessary to give the discs the correct external diameter. Since low-viscosity lacquers are used, the 2p process does not require high pressures, and it can take place at room temperature. Compared with the more conventional thermosetting process, the 2p process has the advantage that no time need be lost in heating the substrate and lacquer and cooling them again. The thin lacquer layer can first be applied between mould and substrate while it is still liquid. The curing does not start until the exposure, and then it is almost instantaneous. An additional advantage of working at room temperature is that there is no thermal shrinkage after curing, and consequently very little stress in the material.

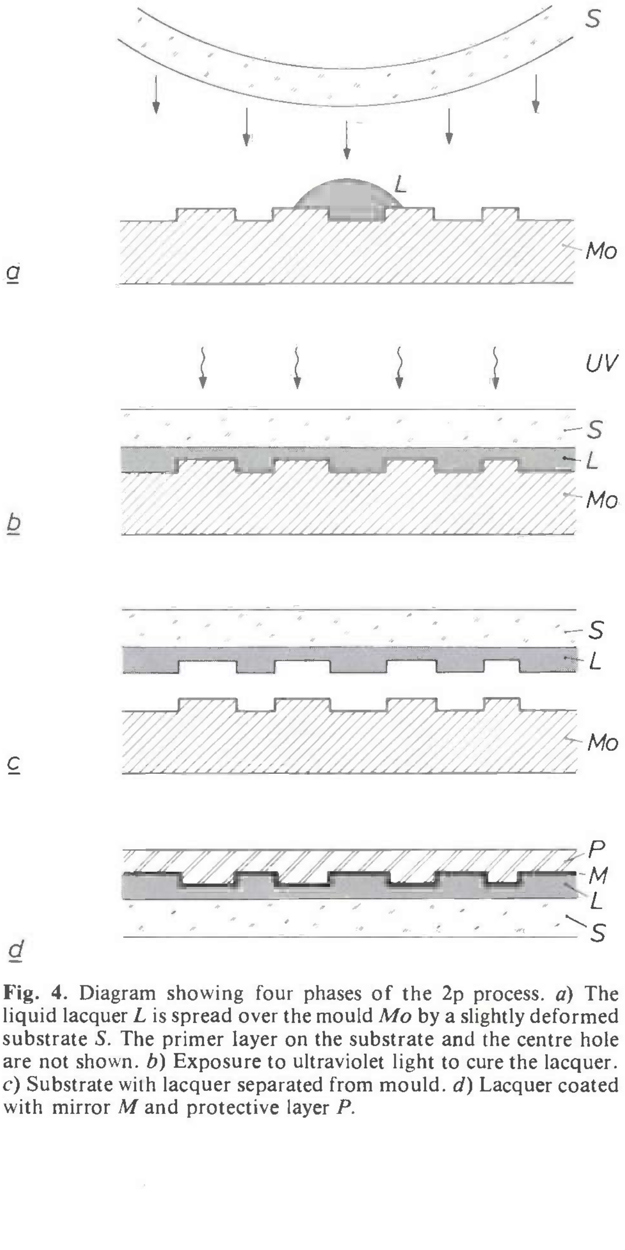


Fig. 4. Diagram showing four phases of the 2p process. *a*) The liquid lacquer *L* is spread over the mould *Mo* by a slightly deformed substrate *S*. The primer layer on the substrate and the centre hole are not shown. *b*) Exposure to ultraviolet light to cure the lacquer. *c*) Substrate with lacquer separated from mould. *d*) Lacquer coated with mirror *M* and protective layer *P*.

Requirements to be met by the LaserVision disc

A video disc on a LaserVision player, operating in accordance with the specifications, must be capable of delivering a good television signal to the television receiver. The specifications of the disc and the player are therefore matched to one another. This means that the disc must satisfy a number of requirements relating to optics, geometry and stability. We shall now take a closer look at these requirements.

Optical requirements

For the stored information to be read properly there must be at least a 75% optical reflection of the laser beam. The absorption and scattering losses that occur as the beam goes through the substrate twice depend strongly on the type of material. The same applies to the losses that arise on reflection from the metal mirror coating. Because a high reflectance is required, very few combinations of materials are suitable for the substrate, 2p lacquer and mirror coating.

Another optical requirement is connected with the use of linearly polarized laser light in the optical system of the player, for separating the incident from the reflected beam. Any change in polarization when the beam returns through the substrate makes this separation less effective, causing a drop in the efficiency of signal detection and an undesired feedback of the modulated light to the laser. This means that the birefringence in the substrate must be no greater than 20°, leading to a further restriction in the choice of materials and in the method of making the substrate.

Geometrical requirements

The specifications laid down for the player and the disc are such as to ensure that any disc can be played well on any player, and also that there is an optimum compromise between the ease of manufacture and production costs of the player on the one hand and of the disc on the other.

The thickness of the substrate was set at 1.25 mm. Thinner substrates are more difficult to make, and moreover with a thickness of 1.25 mm any scratches on the outer surface of the disc are so far outside the depth of focus of the lens of the player that they are no longer troublesome. The tolerance in the average thickness is fairly large, about 100 μm. The specification for the flatness and parallelism of the two surfaces, however, is very tight. Any departure from flatness in the rapidly rotating disc causes vertical movements in the information track. The focus-control system of the player must be able to follow these movements. Translated into the specifications for the focus-control system, the compromise mentioned above corresponds to:

— a maximum vertical deviation of 1050 μm at a frequency $f \leqslant 1.1$ kHz;
— a maximum vertical velocity of 0.18 m/s at $f \leqslant 1.1$ kHz;
— a maximum vertical acceleration of 100 m/s^2 at $f \leqslant 1.1$ kHz;
— a maximum vertical deviation of 2 μm at $f > 1.1$ kHz.

It follows that the curve of the permissible vertical deviation x plotted against the frequency f consists of four segments, which are shown in blue in *fig. 5*. The shaded region indicates the excursion that the focus-control system must be able to follow, as a function of frequency.

To calculate the consequences of this for the disc, we assume that there is a simple harmonic disturbance of wavelength λ along the track on the disc surface, with the amplitude in the axial direction. The frequency at which this disturbance is 'seen' by the focus-control system during read-out depends not only on λ

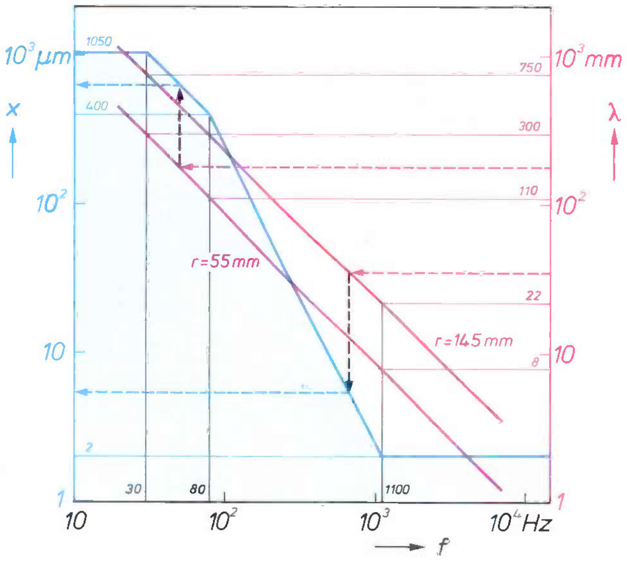


Fig. 5. *Blue:* Permitted vertical amplitude x as a function of the frequency f, as specified for the focus-control system of the LaserVision player. The curve consists of four segments, with a different specification for each segment (see text). The shaded area indicates the excursions that the control system must be able to follow. *Red:* Wavelength λ of an axial disturbance plotted against the frequency f at which the control system 'sees' this disturbance while the disc is being played. The two lines relate to a constant speed of 25 rev/s at the minimum read-out radius (55 mm) and at the maximum read-out radius (145 mm). Combining the red and blue curves indicates the maximum permitted vertical amplitude of a disturbance at wavelength λ and read-out radius r. The dashed lines give two examples of the results of such a combination. The values of f, x and λ corresponding to the changes in the slope of the blue curve are shown along the axes (see Table I).

---

[8] J. S. Winslow, IEEE Trans. **CE-22**, 318, 1976.
D. G. Howe, H. T. Thomas and J. J. Wrobel, Photogr. Sci. Engng **23**, 370, 1979.

[9] J. G. Kloosterboer, G. J. M. Lippits and H. C. Meinders, this issue, p. 298.

but also on the speed of rotation and the read-out radius of the disc. Fig. 5 indicates in red the relation between λ and f at a constant disc speed of 25 rev/s for the minimum and maximum read-out radii (55 and 145 mm). By combining the red and the blue curves in fig. 5 we can read off the permissible vertical amplitude of an assumed sinusoidal disturbance on the disc at a particular read-out radius and a particular wavelength of the disturbance. The principal results are collected in *Table I.*

The specifications are also matched for the radial control system of the player and the radial deviations of the track on the disc. The specifications for the player are:

— a maximum radial deviation of 80 µm at $f \leqslant 2.2$ kHz.

— a maximum radial acceleration of 20 m/s^2 at $f \leqslant 2.2$ kHz.

— a maximum radial deviation of 0.1 µm at $f > 2.2$ kHz.

Fig. 6 indicates in blue and red the relation between the permissible radial deviation y and f and the relation between the wavelength λ of the radial disturbance and f. The consequences for the disc in relation to the permissible amplitude of the radial disturbance are shown in *Table II.*

The specifications for the radial deviations are fairly tight considering the many sources of deviations. These can arise even during the process of making the production moulds. There may be bumps and indentations in the disc, and these can act as a prism and cause radial deflection of the laser light. This is seen by the player as non-circularity of the track. In operation, imbalance in the disc can cause shocks and vibrations in the player.

The tolerance on the outside diameter of the disc is 1 mm. An additional requirement, however, is that the imbalance force during playback should be less than 1.5 N. This imbalance is caused by local thickness variations or more usually by eccentricity. Excessive imbalance can often be corrected by deliberately trimming the outside edge eccentrically.

Table I. Permitted vertical amplitude x of an axial disturbance at the minimum and maximum read-out radius r on a LaserVision video disc played at a constant speed of 25 rev/s (see fig. 5).

λ (mm)		x (µm)
at $r = 55$ mm	at $r = 145$ mm	
> 300	> 750	1050
$300 \rightarrow 110$	$750 \rightarrow 300$	$1050 \rightarrow 400$
$110 \rightarrow 8$	$300 \rightarrow 22$	$400 \rightarrow 2$
< 8	< 22	2

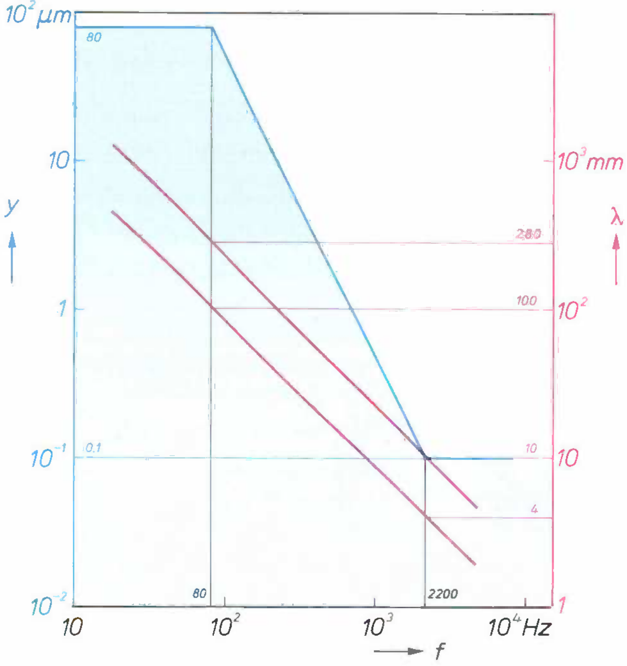


Fig. 6. *Blue:* Permitted radial amplitude y as a function of the frequency f, as specified for the radial control system. The curve here consists of three segments; the shaded area indicates the excursions that the radial control system must be able to follow. *Red:* As in fig. 5, but now for a radial disturbance. The values of f, y and λ corresponding to the changes in the slope of the blue curve are shown along the axes (see Table II).

Table II. As in Table I, but now for the permitted amplitude y of a radial disturbance (see fig. 6).

λ (mm)		y (µm)
at $r = 55$ mm	at $r = 145$ mm	
> 100	> 280	80
$100 \rightarrow 4$	$280 \rightarrow 10$	$80 \rightarrow 0.1$
< 4	< 10	0.1

Stability requirements

The disc must meet its specification immediately after manufacture and during its use by the consumer. The conditions during use are simulated as closely as possible in 'climate tests'. Among the requirements are that use at a temperature of about 40 °C should have no adverse effect on the optical and geometrical characteristics of the disc. The disc must also remain unaffected by the climatic conditions likely to be encountered during transport and storage. Finally, the disc should have an acceptable useful life. This is tested, e.g. in cyclic humidity tests in which ageing is accelerated by subjecting the disc to frequent alternations of temperature (from 20 to 45 °C, and vice versa) and relative humidity (from 50 to 96%, and vice versa).

Choice of materials and process stages

The requirements mentioned above are clearly rather strict for a mass-production process, and obviously restrict the choice of the materials that can be used. This restriction applies not only to the separate components of the disc but also to the complete assembly. This is related to the complicated structure of the disc (fig. 1) and to the considerable differences in the chemical properties of the materials. Changing one of the materials or one of the stages in the process therefore generally requires an appropriate change in one or more of the other materials or process stages. It is consequently not easy to find the optimum production process. It will therefore come as no surprise that we are also investigating and developing other variations of the production process and testing them in pilot production. We shall now describe the choice of materials and the stages in the current production, together with a number of promising variations.

Choice of substrate

An important difference between the 2p process and the mechanical (pressing) reproduction methods is that the substrate in the 2p process serves purely and simply as an inert carrier of the 2p information layer. It would therefore seem that there is considerable freedom in the choice of substrate and in the method of making it. In general terms this is true. The disc blanks can be made from cast, extruded or rolled plastic sheet, by turning or punching. On the information side of the substrate a limited micro-roughness and thickness variation are permissible because of the smoothing action of the 2p lacquer. Some roughness or even small scratches on the outer surface are usually of little significance, since the relatively large substrate thickness brings this surface well away from the focus of the laser beam. The lens of the player has a very large numerical aperture (0.4), so that the laser beam has a relatively large diameter (about 1 mm) when it enters the substrate.

In spite of this large measure of freedom, however, the choice of substrate material remains limited. For economic reasons it is necessary to use plastics, and only three of these will meet the optical and mechanical requirements: polymethyl methacrylate (PMMA), polyvinyl chloride (PVC) and polycarbonate (PC). *Table III* summarizes some of the advantages and disadvantages of these three materials for use as the substrate in the 2p process. The information given is based on our experience with test samples obtained from production and development departments of outside suppliers.

Table III. Properties of polymethyl methacrylate (PMMA), polyvinyl chloride (PVC) and polycarbonate (PC) for possible application as substrate material in the 2p process for the manufacture of LaserVision discs.

Property	PMMA	PVC	PC
absorption at 630 nm	about 5%	about 15%	about 5%
birefringence	acceptable	marginally acceptable, depending on preparation	problematic
glass temperature	about 110 °C	70 °C	140 °C
dimensional stability	sensitive to moisture	vulnerable at high temperature	good
method of manufacture	extrusion, casting, injection moulding	calendering + pressing	injection moulding, difficult because of high glass temperature
price	reasonable high reasonable	attractive	high
compatibility with 2p process	good, but adhesion layer necessary	good, but mirror coating can be attacked by additives and decomposition products	good, but tendency to stress cracking in contact with 2p lacquer

Polycarbonate is not used at present because it is too expensive for the mass production of such large discs and poses problems of birefringence. With PVC as substrate material, problems are mainly encountered with the mirror coating. The optical attenuation of the read-out laser beam in the PVC substrate is fairly high: about 15%. To meet the requirement of at least 75% of total reflection, the mirror coating must then have an inherent reflectance of at least 90%, which is difficult to achieve in practice, because of factors such as degradation during life. When they are combined with a PVC substrate, aluminium and silver coatings can be attacked by substances emanating from the PVC, even with 30 μm of 2p lacquer between the substrate and the metal coating. As Table III shows, PMMA has good optical properties: the absorption at 630 nm is only about 5%, and the birefringence is generally well within the required limits. Because of these properties we have decided for the present to use PMMA as substrate material for the mass-production process.

Compared with the two other substrate materials, PMMA has the disadvantage of being less compatible with the 2p process, because a cured 2p lacquer does not adhere well to a PMMA surface. The substrate surface is therefore given a pretreatment, such as the application of a thin adhesion layer of an acrylic resin.

Another problem with PMMA relates to the water absorption of the material. Unlike PVC, for example, PMMA can absorb a relatively large amount of water vapour (a few per cent by weight), causing the material to swell. Since this is a reversible process, the water content of a PMMA disc is affected by the water content of the ambient air. During the uptake or release of water there are gradients in the water concentration in a PMMA disc, and the associated mechanical stresses can lead to warping of the disc. Fortunately these deformations are largely eliminated when the two disc halves are bonded together to form a symmetrical structure. Nevertheless, careful control of the humidity conditions remains strictly necessary in order to keep the component discs flat during the production process.

Choice of the 2p lacquer

The picture quality of a LaserVision disc depends to a large extent on the properties of the 2p lacquer. The read-out process takes place at the interface between the lacquer layer and the mirror coating, and the depths and lengths of the pits, the slopes of the pit walls, the micro-roughness of this interface and micro-defects in its proximity all play a part in this process. The lacquer must take up the mould information as faithfully as possible, and retain it during the polymerization and afterwards. The cured lacquer layer must also be capable of withstanding the thermal and mechanical stresses during the application of the mirror coating, and in the finished disc it must possess good chemical and mechanical stability.

In addition there are requirements connected with the mass production of the video discs. The lacquer, for example, must have a sufficiently low viscosity to allow a thin layer to be spread out sufficiently fast over the mould surface. It must also polymerize rapidly on exposure to ultraviolet light and the cured lacquer must not adhere to the mould surface. Other conditions relate to matters such as availability, reproducibility and toxicity in the liquid state.

Fig. 7. General view of the 2p machine and related equipment. The machine on the right applies the 2p lacquer in manufacturing the LaserVision discs. The equipment on the left includes a post-exposure unit and a mechanical device for transferring the discs with cured lacquer to a holder.

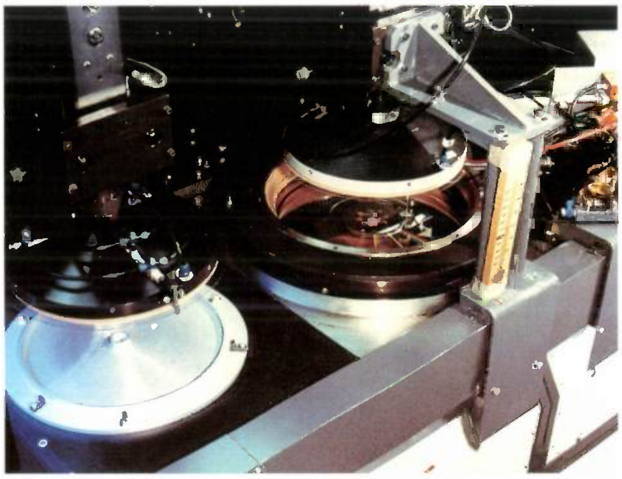


Fig. 8. Photograph showing the disc holder (on the right) for picking up the substrate and spreading out the 2p lacquer. A ring of liquid 2p lacquer can be seen on the mould. The disc holder presses the substrate against the mould, producing a uniform information-carrying layer of lacquer. On the left are the claw device and disc holder that separate the substrate with the cured lacquer from the mould.

The requirements and conditions can be satisfied reasonably well by lacquers that contain one or more acrylates [9]. With a suitable photo-initiator, these lacquers polymerize very rapidly during the ultraviolet exposure. A number of these acrylate layers give a reproduction accuracy that is more than sufficient for disc manufacture. They can also be sufficiently hard, so that the lacquer layer is not deformed on application of the mirror coating. To achieve the required hardness it is usually necessary to have a polymer whose chains are chemically cross-linked by side branches. A suitable polymer can be obtained from a mixture of a diacrylate and a triacrylate. By choosing the correct mix and adding a thinner, the viscosity in the liquid state can be kept sufficiently low. The basic material can also be a single monomer such as hexanediol diacrylate [9].

Application of the 2p layer

Fig. 7 shows the machine designed for applying the 2p layer. After a substrate (with primer layer) has been placed in position, a measured quantity of liquid 2p lacquer is applied and spread out over a nickel mould. First, the area containing the information is exposed to ultraviolet light. Then the superfluous, still liquid part at the unexposed outer edge is removed. The remaining lacquer is then exposed to the ultraviolet light again, to complete the curing, especially at the outer edge, and the substrate with cured lacquer (the 'disc') is removed from the mould.

Some details of the operation of the 2p machine can be explained with reference to *fig. 8*. The substrate is picked up by a 'disc holder', which applies a holding vacuum along the outer edge of the disc and a small excess pressure in the inner area, causing the disc to sag slightly in the middle. A ring of the liquid 2p lacquer is applied around the pin at the centre of the mould, the centring pin. The disc holder is then lowered, and after alignment by means of the centring pin the substrate is pressed flat against the mould. As a result the lacquer is squeezed out to form a circular uniform layer 10 to 30 μm thick. The layer thickness depends on the excess pressure in the disc holder, the rate of spread and the viscosity of the lacquer. After the layer has been spread, the holder is withdrawn and the disc on the mould is transported to an exposure rack consisting of ultraviolet-emitting fluorescent lamps. The two-stage hardening process takes place here in less than 10 seconds. The disc and the mould are then transported to the separation position, where a claw device and a second disc holder separate the disc from the mould. Outside the 2p machine all the discs are given a final ultraviolet exposure directly on to the 2p lacquer to complete the curing process. The mirror coating can then be applied.

Depending on factors such as the viscosity and the curing behaviour of the lacquer, the total cycle time of the 2p machine is at present 30 to 40 seconds. A considerably shorter cycle time seems feasible, particularly since it may be possible to reduce the curing time to about 1 second.

Depositing the mirror coating

The mirror coating should have a sufficiently high reflectance at the read-out wavelength, since at least 75% of the incident laser light should be reflected. As we have seen, the optical attenuation in a PMMA substrate is about 5%, so that the inherent reflectance of the mirror coating must be at least 80%. For this reason, and in connection with material costs, stability and reactivity, the choice of material is limited to the metals aluminium, silver and copper. These have theoretical reflectances of 85, 99 and 95%, respectively, at the read-out wavelength. These values also apply generally to thin layers with a thickness of only a few tens of nanometres.

Until now little attention has been paid to copper as a possible mirror material, mainly because of the attractive appearance of the disc with an aluminium or silver layer. At the start of disc production it was decided to use vacuum evaporation (vapour deposition) as the method of applying the metal coating. An evaporated silver layer, however, has poor adhesion to the 2p surface, so that a finished disc could fracture at this interface. Although this problem can be solved by chemical treatment of the 2p surface, extra stages in the production process would be necessary. Aluminium, on the other hand, adheres well to the 2p surface, and this material has therefore been chosen for the time being.

Fig. 9. Photograph of the evaporation area (above) and a carrousel holder (below) for the deposition of aluminium on LaserVision discs.

Batches of about 120 discs are aluminized on a rotating carrousel holder (*fig. 9*) by evaporation from simple aluminium-coated resistance elements. In this deposition process a problem arises because of the use of PMMA as substrate material. Owing to its water-vapour absorption, PMMA in vacuum desorbs a great deal of water vapour for some considerable time. Evaporation of aluminium at an insufficiently low pressure leads to a lower reflectance, owing to the reaction between water vapour and the growing layer. It was therefore necessary to design special evaporators with very large liquid-nitrogen-cooled cryopump surfaces, that would enable a pressure of 10^{-3} Pa to be reached easily in a short time.

Good mirror coatings can in fact be made by evaporation, but the batch-loading method is not easily integrated into the production process, which is otherwise continuous. The large carrousel holders have to be loaded and unloaded, and for each batch a relatively long time is required for pumping down the evaporation chambers and readmission of air after deposition. Labour-intensive maintenance is also necessary to ensure that dust in the chambers, stirred up during pumping and readmission of air, does not give rise to pinholes in the mirrors. For these reasons two alternative metallization techniques are now in development, which may lead to more efficient production.

Alternative metallization techniques

A suitable metallic mirror can also be obtained by 'electroless' silver deposition, a wet chemical process in which the entire surface is coated with a thin layer of silver. A process of this type has long been used for producing glass mirrors. In the electroless silver deposition on a cured 2p lacquer the surface of the lacquer is simultaneously sprayed with an ammoniacal aqueous solution of a silver salt and a solution of a suitable reducing agent. When the two solutions mix on the surface metallic silver is formed. As with an evaporated silver coating, the adhesion to the 2p surface is poor. The surface is therefore given a pretreatment with an aqueous solution of an organic compound that modifies the surface of the 2p lacquer. After further treatment with an inorganic agent containing tin to increase adhesion, the deposition of the silver is started.

Since all the stages in this method of metallization consist of liquid-spraying operations, it was possible to develop a continuous production machine in which the discs undergo all the required operations sequentially on a conveyor belt. A prototype of this machine is illustrated diagrammatically in *fig. 10*, and a photograph is shown in *fig. 11*.

This metallization method takes on average much less time per disc than evaporation. Continuous rinsing of the surface with liquids almost completely prevents the occurrence of pinholes in the silver coating, as required for the LaserVision discs. *Fig. 12* shows a transmission-electron-microscope (TEM) photograph of a silver coating. For this photograph the adhesion treatment was omitted, so that the metal coating could easily be separated from the 2p lacquer and mounted as a separate film in the transmission electron microscope. The photograph covers an area somewhat lar-

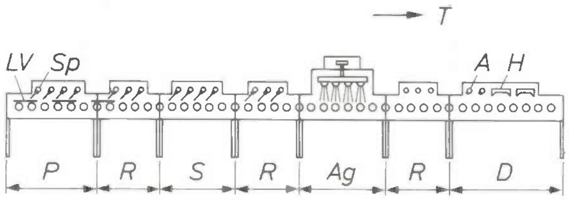


Fig. 10. Schematic prototype of machine for electroless silver deposition. *LV* LaserVision disc on a conveyor belt for transport *T*. *P* pretreatment. *R* rinsing. *S* sensitization. *Ag* silver deposition. *D* drying. *Sp* spray nozzle. *A* air blade. *H* heater element.

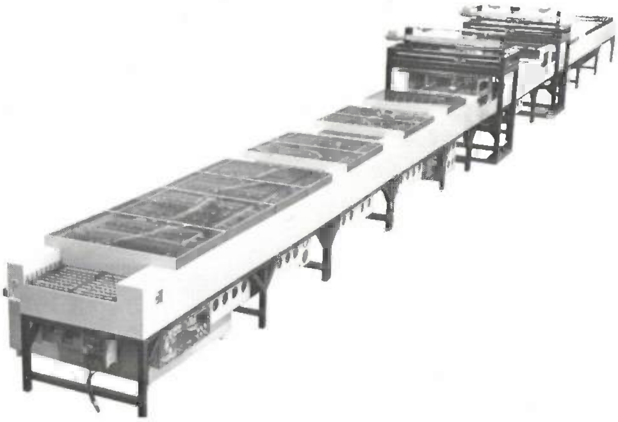


Fig. 11. Photograph of the machine for electroless silver deposition. This machine incorporates two metallization stations.

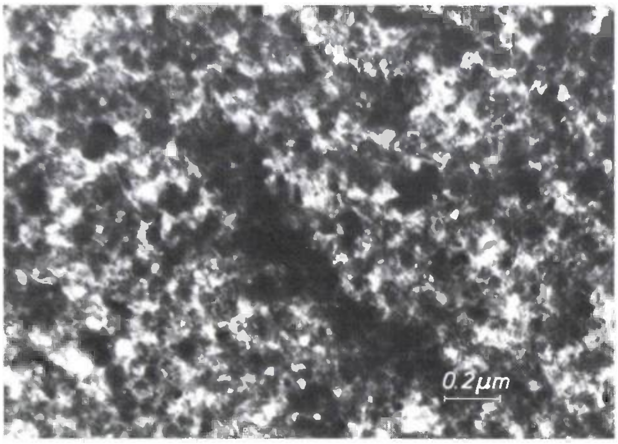


Fig. 12. Transmission-electron-microscope (TEM) picture of a layer obtained by electroless silver deposition on a cured 2p lacquer with a LaserVision pattern. The walls of the pits are also uniformly coated with silver.

ger than one pit, and shows the small crystallites that form the coating. It can be seen that the coverage is uniform, even on the walls of the pits.

A second alternative metallization technique is the method of 'magnetron sputtering' from a cold solid target by means of bombardment with ions (usually argon ions) [10]. At an argon pressure of about 10^{-1} Pa and a sufficiently high direct voltage, a discharge is formed between a target, acting as cathode, and an anode. With a magnetic field, maintained by permanent magnets behind the cathode, a concentrated discharge plasma is produced immediately above the target surface. Ar^+ ions at an energy of 300 to 500 eV can be extracted from the plasma, and these ions bombard the target surface and sputter its material. The disc to be coated is situated directly opposite the target and outside the plasma region.

Fig. 13 is a diagram of the continuous sputtering machine specially designed for mass production. The design makes allowance for the high water desorption of PMMA. A photograph of the machine is given in *fig. 14*. The production rate is determined mainly by the sputtering time, and not by the time taken for loading and unloading, so that the metallization is again much more efficient than with evaporation. It also allows more freedom in the choice of the mirror material. Binary and ternary alloys can be applied, some of which have desirable properties for LaserVision applications, including high stability and low internal stresses. Another advantage is the generally better adhesion to the cured 2p lacquer. It is even possible to apply silver coatings that adhere well to the 2p lacquer when certain gases are added to the argon plasma.

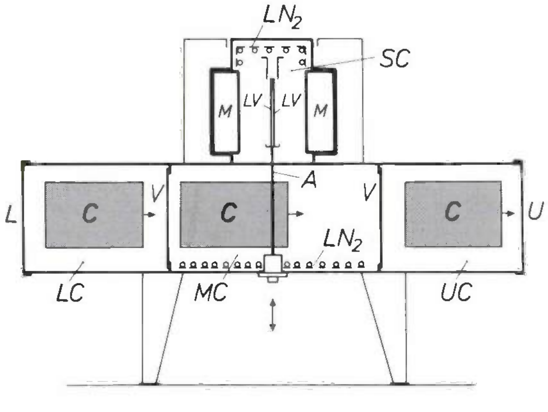


Fig. 13. Magnetron sputtering machine for mass production. *L* loading door. *LC* loading chamber. *C* cassette for discs. *V* valve. *MC* magazine chamber. LN_2 cryopump surface cooled by liquid nitrogen for pumping water vapour. *M* magnetron. *LV* LaserVision disc. *UC* unloading chamber. *A* lifting arm. *SC* sputtering chamber. *U* unloading door. The vacuum pumps for the four chambers are not shown.

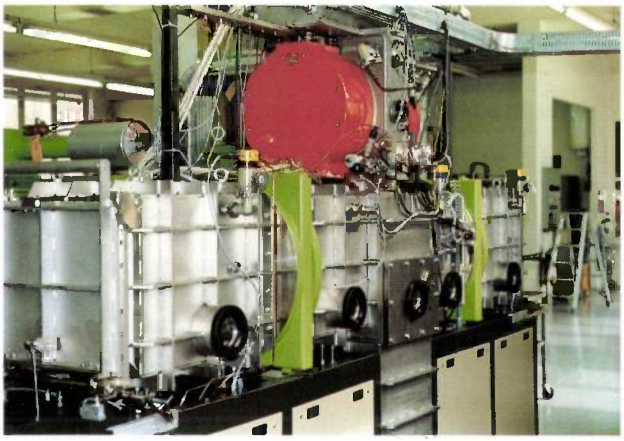


Fig. 14. Photograph of magnetron sputtering machine with the chambers indicated in fig. 13. The magazine chamber is in the centre, between the two green valve housings; the sputtering chamber is above it, with the red enclosures for the two magnetrons.

Finishing operations

After the metallization the sides of the disc are ready for use. At this stage the electro-optical characteristics and the signal quality of the separate sides can be determined, if necessary. First the plastic protective layer is sprayed on to the mirror coating. This layer is also the base for the adhesive used for bonding the two discs back-to-back to form the final double-sided video disc. Both sides are then sprayed with an acrylic-based dispersion contact adhesive, which is left to dry until a rough 'orange-peel' texture forms. This microstructure is necessary to allow the escape of air trapped during assembly, which might introduce local deformations and hence unacceptably large vertical accelerations during playback. The danger of entrapping air can also be avoided by assembling at low pressure.

After a pressing operation over the entire surface, the inside and outside edges of the double disc are again firmly pressed together to ensure a reliable seal, mainly to prevent the penetration of moisture, which could affect the back of the mirror coating. If necessary the disc is balanced by turning the outer edge eccentrically. Finally the labels are applied to both sides, and the disc is inspected, tested and packed.

Summary. The mass production of the video discs for the Philips LaserVision system, now on the market in Europe, is carried out at Blackburn, England. The discs are manufactured in a photopolymerization process: a liquid polymerizable lacquer is cured on a mould by exposure to ultraviolet light, so that the picture and sound information of the mould is imprinted in the lacquer. A complete video disc is formed from two component discs bonded together; each side consists of a transparent substrate, a primer layer, a cured lacquer layer containing the information, a metal mirror coating and a protective layer. The materials chosen for these layers and the methods used in applying them permit video discs to be produced that comfortably satisfy the exacting requirements of the LaserVision system.

---

[10] See for example J. J. Scheer and J. Visser, Philips tech. Rev. **39**, 246, 1980.

Photopolymerizable lacquers for LaserVision video discs

J. G. Kloosterboer, G. J. M. Lippits and H. C. Meinders

Introduction

As described in the previous article [1], the manufacture of LaserVision discs by the photopolymerization (2p) process places some very exacting requirements on the lacquer in which the information is stored. Some of these requirements, such as a high curing rate, low viscosity and good adhesion to the substrate, relate to the application in the 2p process, while others are connected with the specifications of the discs, e.g. the dimensional stability, durability and lack of odour. In addition, production technicalities such as availability, purity, constancy of composition and price are also important in the ultimate choice of lacquer.

A lacquer that meets all the requirements is not easy to find, largely because some of the requirements are more or less conflicting. For example, it must be easy to release a cured lacquer from a metal mould (sometimes called a 'stamper') , whereas the lacquer must adhere well to the metallic mirror coating applied later. There are two ways of achieving an acceptable compromise. One way is to look for a mixture of different monomers, each providing one or more of the desired properties. This entails an investigation of the dependence of the process and product properties on the composition. Another way is to make a careful study of the polymerization process and the relation between molecular structure and chemical behaviour, and in this way to try and find a monomer that combines as many desirable properties as possible.

In the investigation described in this article both approaches were adopted, the first mostly at the Centre for Metallurgical Chemistry and Lacquers (CMCL) of the Philips Plastics and Metalware Factories (PMF), the second mostly at Philips Research Laboratories. Both approaches have led to the manufacture of playable discs of good quality. It is not yet appropriate to draw any conclusion as to which lacquer is the best: process development is still in full progress and a small change in the 2p process may in turn necessitate the use of a different lacquer composition. Nevertheless, the information obtained already enables us to anticipate new developments.

In this article we shall first give a short general description of photopolymerization. We shall consider the mechanism, the choice of substances to be used and the methods of monitoring the polymerization reaction. We shall then discuss the search for suitable lacquers made from mixtures of monomers, and finally the search for suitable single-component lacquers.

Photopolymerization

In polymerization a large number of small molecules, monomers, are linked together to form chains of macromolecules [2]. The linking can take place by condensation or by addition. In condensation the formation of the macromolecules is generally accompanied by the formation of one or more by-products, e.g. water. During the reaction, dimers are first formed, then trimers, tetramers, and so on, which can also react with one another. It is only towards the end of the reaction that this step-by-step process leads to the formation of very long polymer chains of high molecular weight. Addition polymerization, on the other hand, proceeds in the form of a chain reaction, in which a chain, once started, keeps on growing through the addition of one monomer after another. No by-products are formed in this reaction. To start the chain growing, molecules with an unpaired electron (radicals) can be used. These can arise from the dissociation of an activating substance, called the initiator. When this dissociation is produced by the action of visible or ultraviolet light, the process is

---

Dr J. G. Kloosterboer and Drs G. J. M. Lippits are with Philips Research Laboratories, Eindhoven; Dr H. C. Meinders is with the Philips Plastics and Metalware Factories (PMF), Eindhoven.

referred to as photopolymerization [3]; when the dissociation is produced by heating the process is called thermal polymerization.

For replication processes, addition reactions are clearly preferable to condensation reactions, since no by-products are formed and, if a photosensitive initiator is used, the reactions are easy to control externally, since the polymerization does not start until light is absorbed by the initiator. The addition reactions controlled by light are also extremely efficient: the absorption of a single photon by the initiator can trigger the growth of a chain of 1000 to 10 000 monomer links. Another important advantage is that the solutions of photo-initiators in monomers used for photopolymerization are stable in the dark, unlike solutions of thermal initiators in monomers. The photosensitive solutions can therefore be used without any danger of spontaneous reaction and explosion during transport and storage.

The mechanism

The photopolymerization of a monomer M, started by the initiator AB that supplies the radicals $A^{\bullet}$ and $^{\bullet}B$ can be represented schematically as follows:

$$\begin{array}{lll} AB \xrightarrow{h\nu} A^{\bullet} + {}^{\bullet}B & & \textit{dissociation} \\ A^{\bullet} + M \rightarrow AM^{\bullet} & & \textit{initiation} \\ AM^{\bullet} + M \rightarrow AMM^{\bullet} & & \textit{propagation} \\ AMM^{\bullet} + M \rightarrow AMMM^{\bullet}, & & \textit{propagation} \\ \quad \text{etc.} & & \end{array}$$

Once the radical $AM^{\bullet}$ has been formed in the initiation process, the reaction proceeds by itself. If the original material contains different monomers, these can be incorporated in the same chain; this is referred to as 'copolymerization'.

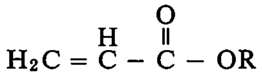
In theory a single radical $A^{\bullet}$ should be sufficient to make all the monomer molecules react together to form an enormously long single chain. This does not happen, because reactive radical end-groups are deactivated by termination, for example when two radicals meet:

$$\begin{array}{ll} AM..M^{\bullet} + {}^{\bullet}B \rightarrow AM..MB & \textit{termination} \\ AM..M^{\bullet} + {}^{\bullet}M..MA \rightarrow AM..MM..MA & \textit{termination} \end{array}$$

The two unpaired electrons thus form a covalent bond and a non-reactive polymer molecule is produced. Moreover, the growth can also be inhibited or even completely suppressed. This happens, for instance, in the presence of dissolved oxygen, because this reacts with the radicals and the resulting peroxy radicals are not highly reactive. After the oxygen and other inhibitors that may be present have been converted, the rate-determining step of the polymerization process is the initiation. Propagation takes place almost of its own accord: the process has a low activation energy and a relatively large amount of heat is released (up to 800 J/g). After initiation, a chain can therefore grow very fast until the point of termination is reached. The length a chain can grow to is determined by the probability of termination. This probability depends on the concentration of radicals and hence on the intensity of the light. A high intensity gives rise to the formation of relatively short chains.

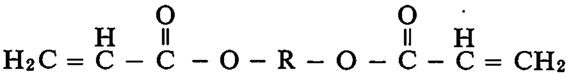
Choice of monomers and photo-initiators

For a monomer, or class of monomers, to be used in the 2p process it is necessary to satisfy requirements with regard to rate of polymerization, separation from the mould, adhesion of the mirror coating, dimensional stability, etc. If the process is to be efficient, the polymerization rate must be high. Fast polymerization reactions are particularly easy to obtain with acrylates, which are esters of acrylic acid of the general formula:



$$H_2C = \overset{H}{C} - \overset{\overset{O}{\|}}{C} - OR$$

where R is an arbitrary group that does not significantly affect the mechanism of the polymerization. This is a justification for insisting on the speed requirements: without too great a sacrifice of polymerization rate it is possible, with a suitable choice of R, to meet the other requirements of the 2p process as well. Thus, a lacquer can acquire high dimensional stability when R has an acrylate group on each side:



$$H_2C = \overset{H}{C} - \overset{\overset{O}{\|}}{C} - O - R - O - \overset{\overset{O}{\|}}{C} - \overset{H}{C} = CH_2$$

Molecules with such a structure will introduce cross-links between different chains. This cross-linking leads to the formation of a three-dimensional network.

The photo-initiator decomposes into radicals when it is irradiated by light in a particular absorption band of the molecule. For efficient initiation the location of this band should match the emission spectrum of the light source as closely as possible. Both should also be situated in the wavelength range above 300 nm, in

---

[1] H. C. Haverkorn van Rijsewijk, P. E. J. Legierse and G. E. Thomas, this issue, p. 287.

[2] P. J. Flory, Principles of polymer chemistry, Cornell University Press, Ithaca, New York, 1953.
G. Odian, Principles of Polymerization, 2nd edn, Wiley, New York 1981.

[3] In a narrower sense this term is used only when a photon is necessary for every link of a monomer. Chain reactions that are only initiated by light are then referred to as light-induced reactions. In this article, however, we use the term photopolymerization in the broad sense, that is to say when light is necessary in one way or another for the polymerization process.

which the acrylate monomers themselves have extremely low absorption. On the other hand, to produce a colourless product the initiator should absorb the minimum amount of visible light (400-700 nm). Some photosensitive aromatic ketones have an absorption maximum at about 350 nm and therefore meet these requirements. These compounds are somewhat sensitive to the blue-violet part of the visible spectrum, but in a 'yellow room' the lacquers in which they are dissolved can safely be handled without undesired polymerization. An example of a suitable initiator is 1,1-dimethoxy-1-phenylacetophenone (DMPA). On irradiation with light at about 350 nm one of the products is the benzoyl radical (*fig. 1*), which is highly reactive and an efficient initiator for the polymerization of acrylates.

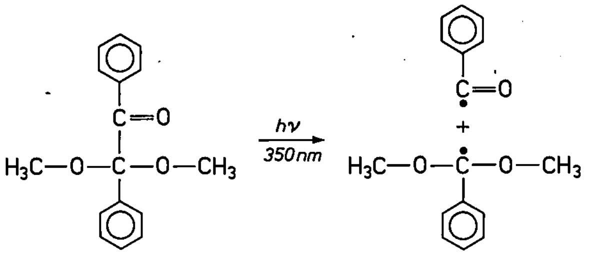


Fig. 1. Decomposition of the photo-initiator 1,1-dimethoxy-1-phenylacetophenone (DMPA) into a benzoyl radical and a dimethoxybenzyl radical by irradiation with ultraviolet light at a wavelength of 350 nm.

Monitoring the reaction

The progress of a polymerization reaction can be monitored by a number of methods: see *Table I*. Classical methods, such as measuring the volume shrinkage (dilatometry), determining the increase in viscosity and weighing the deposited polymer provide information about a macroscopic property of the material. This is also true for the more recent method of gel-permeation chromatography, in which particles of different molecular weight can be separated and the molecular-weight distribution determined. Most of these methods are not very suitable for monitoring a reaction through to a high degree of conversion, especially when there is considerable cross-linking. In such a case a method such as microcalorimetry, in which the heat of reaction is determined as a function of time, is more suitable. With the spectroscopic techniques mentioned in Table I it is possible to make measurements on a molecular scale. The concentration of unreacted $C=C$ bonds can be determined by measuring the ultraviolet or infrared absorption and the Raman emission (inelastic light scattering) due to the monomer and polymer molecules. With this method the progress of a polymerization reaction can also be monitored right through, even when there is cross-linking.

In our investigation Raman spectroscopy and microcalorimetry have been very useful. For fast routine measurements of reactivity a modern version of dilatometry has been particularly appropriate. A thin layer of liquid lacquer is introduced between two glass plates and then irradiated. By measuring the reduction in thickness of this sandwich as a function of time a measure of the reaction rate is obtained. In this way reactions with shrinkage half-value times of less than one second can be monitored. As an example we shall now briefly discuss the method of monitoring a reaction by means of microcalorimetry.

During the polymerization of acrylates a relatively large amount of heat is generated. When one type of reaction (in our case propagation) is dominant, the heat production is proportional to the polymerization rate, i.e. the number of monomers converted in unit time. This also applies to mixtures of acrylates, since all acrylate molecules give virtually the same heat of reaction per acrylate group. The polymerization rate v is proportional to the concentration of radicals and monomers. In the steady state the radical concentration $[R^\bullet] = \sum_i [AM_i^\bullet]$ can be assumed to be constant: in unit time the dissociation of the initiator produces about as many radicals as disappear by termination. The reaction rate is then proportional to the monomer concentration [M] and will decrease exponentially with time: $v = -d[M]/dt \propto [R^\bullet][M]$.

In a dilute solution of a monomer in an inert solvent this relation is indeed found. At higher monomer concentrations, however, a complication occurs, because the viscosity shows a marked increase during the reaction. This seriously inhibits the diffusion of large macroradicals, while the diffusion of the much smaller monomer molecules is hardly affected. Termination, generally a reaction between two large

Table I. Some methods for monitoring a polymerization reaction.

Method	Measurement of:
Dilatometry	Volume shrinkage
Viscosimetry	Increase of viscosity
Gravimetry	Weight of polymer after separation from monomer by precipitation
Gel-permeation chromatography	Molecular weight distribution of formed polymer
Microcalorimetry	Heat of reaction
Refractometry	Increase in refractive index
$C=C$ spectroscopy	UV absorption (layers to 1 μm) IR absorption (layers to 10 μm) Raman emission (inelastic light scattering)

macroradicals, is therefore much more strongly suppressed than propagation, which requires a collision between a large macroradical and a small monomer molecule. In this way, for each chain initiated there will be many more monomer molecules converted, and for a constant initiation rate the reaction rate will therefore increase steeply. This effect is called auto-acceleration and is also known as the Trommsdorff effect [2].

To illustrate this effect *fig. 2* gives a plot of the relative reaction rate against time for the formation of polymethyl methacrylate, also known as Plexiglas or Perspex. After about 100 minutes, with a conversion of about 20%, a very marked auto-acceleration peak occurs. Acrylates give such a peak in the rate right at the start of the reaction. Some acrylates, e.g. ethyl acrylate, even have two different acceleration peaks (fig. 2); the explanation of this effect does not come within the scope of this article [4].

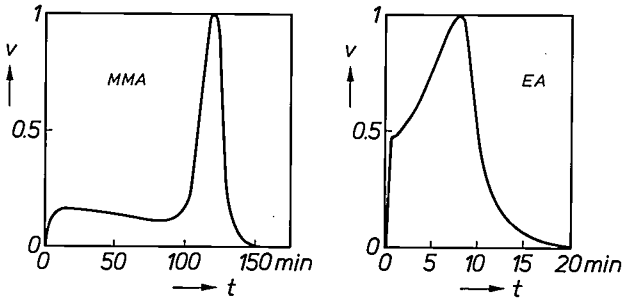


Fig. 2. Reaction rate v (in arbitrary units with 1 as maximum) as function of the time t, for photopolymerization of methyl methacrylate (MMA) and ethyl acrylate (EA) at 20 °C.

Copolymerization

Very many polymers used in practice are copolymers, which result from polymerization of different monomers to form a single type of chain or a single network. When a mixture of monomers is used and its composition is taken as a variable, considerable freedom of choice is obtained for certain properties of the polymer, making it possible to tailor a product to a particular application. This is of great interest when a large number of requirements have to be met at the same time, as in the video disc.

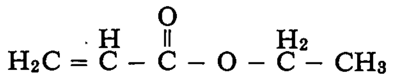
The reaction of a mixture of monomers is often complicated. In copolymerization two different monomers M_1 and M_2 are not incorporated in the network at random if they do not have exactly the same chemical reactivity to the radicals $M_1^{\cdot}$ and $M_2^{\cdot}$. In the extreme case where $M_1^{\cdot}$ and $M_2^{\cdot}$ have a distinct preference for M_1 and M_2, respectively, 'block' copolymers are formed in which there are small regions of poly-M_1 and poly-M_2. On the other hand, if $M_1^{\cdot}$ has a distinct preference for M_2 and $M_2^{\cdot}$ for M_1, then 'alternating' copolymers are formed. The reactivity ratios are known only for a few monomer pairs, and are difficult to determine in cross-linking systems. When the monomers react at different rates, the composition of the as yet uncured part of the mixture will also change during the reaction, as will also the composition of the polymer formed later. This requires accurate optimization of the mixture. To obtain a system that could be studied more easily, we also investigated the possibility of making good video discs with a single monomer, by means of 'homopolymerization'. During the polymerization of such a single-component lacquer there are of course no differences in reactivity and the composition of the polymer formed at different times is constant.

The search for a suitable mixture

Because of the many possible variations of the R group there are many acrylates and hence very many possible different mixtures. The actual number, however, is considerably reduced when account is taken of the requirements for dimensional stability, shrinkage, adhesion and hardness. Our second selection was based on the required viscosity and rate of polymerization. The possible variations in R that we considered related to factors such as the length, and hence the flexibility of the molecule, and the number of C=C bonds and polar groups.

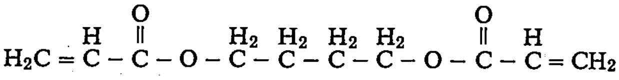
Selection based on dimensional stability, shrinkage, adhesion and hardness

One of the quantities that affects the dimensional stability of an acrylic polymer is the functionality f of the monomer. The value of f is equal to the number of molecules with which a monomer molecule can form direct bonds. A monomer with low functionality ($f = 2$), is ethyl acrylate:



$$H_2C=\overset{H}{C}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-CH_3$$

This monomer gives a rather unstable, rubbery polymer with long flexible chains and few cross-links. A monomer with a higher functionality gives more cross-links on polymerization, resulting in increased dimensional stability. An example of this is 1,4-butanediol diacrylate (BDDA), a monomer that can be considered to be built up from two molecules of ethyl acrylate:

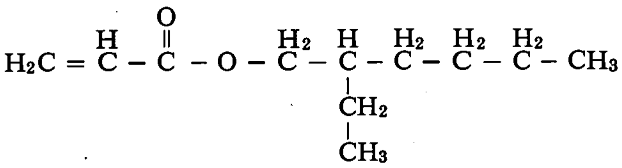


$$H_2C=\overset{H}{C}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-O-\overset{\overset{O}{\|}}{C}-\overset{H}{C}=CH_2$$

---

[4] H. J. L. Bressers and J. G. Kloosterboer, Polymer Bull. 2, 201, 1980.
J. G. Kloosterboer and H. J. L. Bressers, Polymer Bull. 2, 205, 1980.

BDDA not only has a higher functionality ($f = 4$), but because the molecule is relatively small, it also has a large number of C=C bonds per unit volume. This results in a dense network, and hence in a stiff, not very flexible material. In addition, there is strong polymerization shrinkage, amounting to about 15% of the volume. A lacquer layer of thickness 50 µm, for example, will cause warp in a 1 mm plastic substrate. If the substrate is made of glass, and of the same thickness, the lacquer layer will crack. The flexibility can be substantially increased by adding a bulky 'auxiliary' monomer with low shrinkage, e.g. 2-ethylhexyl acrylate (EHA):



$$H_2C = \overset{H}{C} - \overset{\overset{O}{\|}}{C} - O - \overset{H_2}{C} - \underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{\overset{H}{C}} - \overset{H_2}{C} - \overset{H_2}{C} - \overset{H_2}{C} - CH_3$$

Besides the concentration of C=C bonds, it is also possible to consider the fraction of saturated hydrocarbon groups k, which is a measure of the groups not taking part in the reaction as a percentage of the total volume of the lacquer.

With the aid of f and k the available monomers can be mapped as in *fig. 3a*. On the right-hand side of the diagram are the soft, paraffin-like monomers with $R = CH_3(CH_2)_n-$, and on the left are BDDA, etc. Above are a few triacrylates ($f = 6$) and one tetra-acrylate ($f = 8$), which, because of the low flexibility of their polymers, are even less useful in the pure form than BDDA. Tri- and tetra-acrylates with long chains of bulky groups do exist, but they are not available in a sufficiently pure state and are therefore not included in the figure.

The values of f and k of a few mixtures, and the monomers from which they are built up, are given in fig. 3*b*. This figure also indicates whether the cured lacquer can easily be released from the mould and whether there is good adhesion to the substrate. If the disc is to be released easily the cured product must contain no strongly polar groups such as $-OH$, $-SH$, and $-\overset{\overset{O}{\|}}{C}-OH$, because these groups can cause strong adhesion to certain metals. They can also produce corrosion of the mirror coating that will be applied later. Some mixtures, especially those of monomers with a long aliphatic chain, cannot be used because they do not adhere well even to a pretreated substrate.

A further constraint arises from the need to take account of the required hardness of the polymer; see fig. 3*c*. When a mirror coating is deposited by evap-

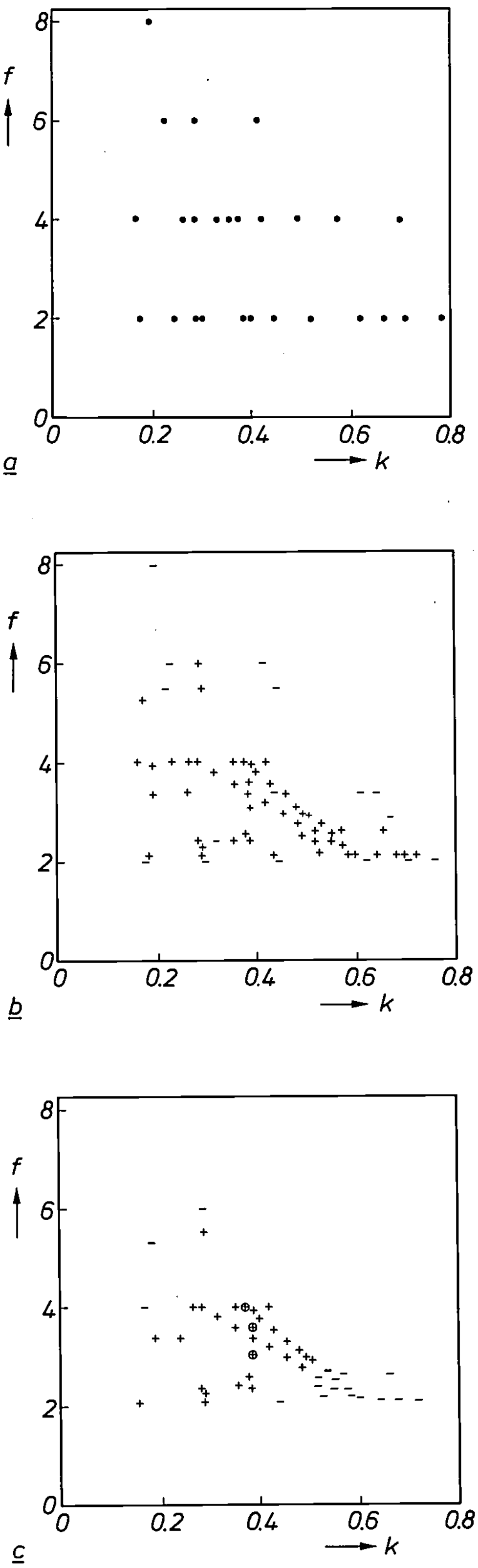


Fig. 3. Saturated hydrocarbon fraction k and functionality f of commercially available acrylate monomers (*a*), and for a number of mixtures composed from them (*b* and *c*). In *b* there is an indication of whether, after curing, good adhesion is obtained at the substrate and whether the layer separates readily from the mould; + yes, − no. In *c* there is a further selection, depending on whether the material remains bright on metallization; + yes, − no. The indications for two mixtures and a single-component layer that will give good video discs are ringed.

oration or sputtering, stresses occur in the metal layer, and on a soft lacquer these could cause shear and deformation. This shows up as a wave pattern on the surface of the lacquer (*fig. 4*) and produces a milky discolouration. A good impression of the hardness of a cured lacquer is obtained by measuring the depth of indentation produced by a diamond point under a standard load. In *fig. 5* the indentation depth in the polymer is plotted against the BDDA content for mixtures of EHA and BDDA. The hardness increases with the amount of BDDA in the mixtures. In practice it is generally found that no problems are encountered for indentations of less than 3 to 4 μm, and that, with carefully controlled metallization conditions, good discs can also be made with even softer lacquers.

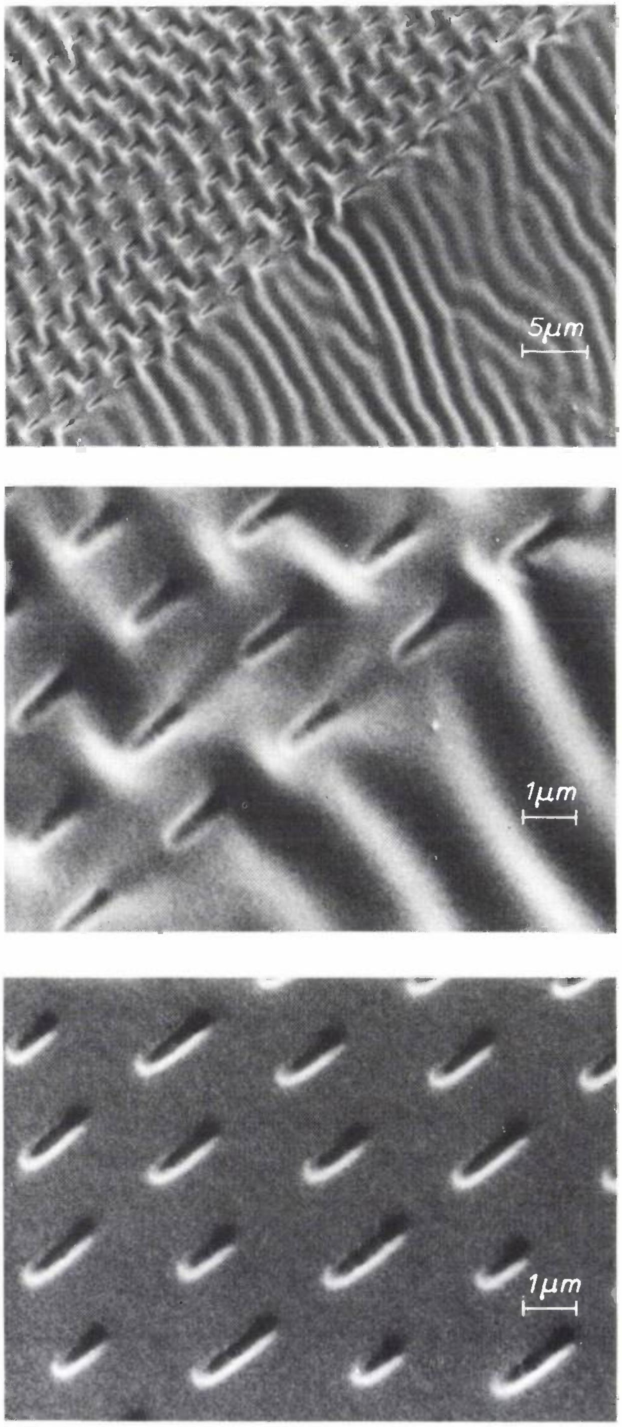


Fig. 4. Scanning-electron-microscope (SEM) pictures of the LaserVision pattern after metal deposition on a lacquer of a mixture of 2-ethylhexyl acrylate (EHA) and 1,4-butanediol diacrylate (BDDA). The upper photograph (magnification 2500×) and the photograph in the centre (magnification 10 000×) were obtained with the composition 80% EHA, 20% BDDA. After metallization the soft lacquer appears as a wave pattern. The lower photograph (magnification 10 000×) was obtained with the composition 20% EHA, 80% BDDA. Since the lacquer substrate is sufficiently hard, there is no wave pattern.

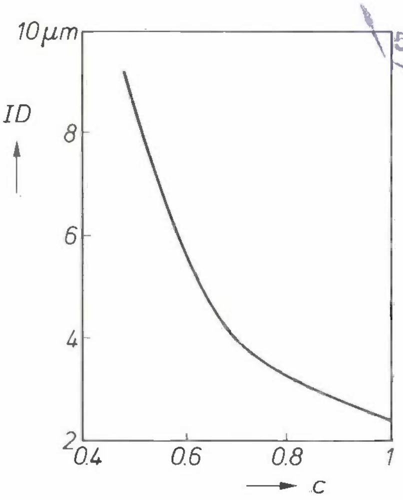


Fig. 5. Indentation depth *ID* of a standard diamond point in cured mixtures of EHA and BDDA, as a function of the BDDA content *c*. When *c* is increased the indentation depth decreases as a result of an increase in the hardness of the cured lacquer.

Selection based on viscosity and reactivity

For the 2p process the viscosity of the still-liquid layer should preferably be between 5 and 15 mPa.s. If the viscosity is too low, the lacquer does not spread out uniformly. If the viscosity is higher than 15 mPa.s, air bubbles can easily be enclosed at high production rates. Furthermore, with the method employed, it is difficult to make polymer layers that are uniformly thick from viscous lacquers.

To achieve a high production rate the reactivity of the monomer must be as high as possible. *Table II* gives the viscosity and the relative reactivity of a number of potentially useful monomers, and also the indentation depth of a diamond point in the polymer.

Because of their high viscosity, triacrylates cannot be used as the principal component of a mixture. On the other hand there are various diacrylates that do have a suitable viscosity. Of these, tripropylene glycol diacrylate (TPGDA) has the greatest reactivity. Some mixtures of TPGDA and monomers with one C=C bond appear to be even more reactive, as do mixtures

Table II. Properties of some single-component lacquers [a].

Monomer	Abbreviation	Viscosity at 23 °C (mPa.s)	Relative reactivity [b]	Indentation depth [c] (μm)
diacrylates:				
diethylene glycol diacrylate	DEGDA	7.8	1.06	1.9
polyethylene glycol diacrylate	PEGDA	24.3	*1.00*	10
dipropylene glycol diacrylate		8.6	2.10	2.3
tripropylene glycol diacrylate	TPGDA	12.3	3.00	3.4
hexanediol diacrylate	HDDA	6.7	2.98	2.8
3-methylpentanediol diacrylate		6.6	1.33	3.3
Ebecryl 180 (UCB)		25.8	1.54	2.4
4160 (Diamond Shamrock)		17.0	3.07	3.5
triacrylates:				
trimethylolpropane triacrylate	TMPTA	107	3.60	1.5
4094 (Diamond Shamrock)		172	3.44	2.3

[a] 96% monomer + 4% photo-initiator, irradiated with TL05 lamp.

[b] Determined by shrinkage measurements. The value for PEGDA is taken equal to 1.00.

[c] For a diamond point in the cured lacquer. A small penetration depth corresponds to a high hardness of the lacquer.

of TPGDA and some triacrylates, e.g. trimethylolpropane triacrylate (TMPTA); see *Table III.*

The reactivity of a mixture of TPGDA and TMPTA can be further increased by the addition of N-vinylpyrrolidone (NVP); see *Table IV.* In this case there is obviously a synergetic effect, because pure NVP polymerizes so slowly that the progress of the reaction cannot be monitored by the conventional shrinkage measurement. The cause of the accelerating action of NVP is not yet entirely clear. It could be that the effect is related to the ring structure of NVP, since N-methylpyrrolidone also causes an accelerated reaction. Dimethyl acetamide, which also has a tertiary nitrogen atom next to a carbonyl group, but no ring structure, has the opposite effect of reducing the reactivity, probably through dilution of the lacquer. Of course, the two other substances also function as diluents, but evidently the accelerating effect predominates.

Some results

Various mixtures of TPGDA, TMPTA and NVP meet all the requirements of the 2p process and are suitable for use in the mass production of video discs. After curing, the lacquers do not give off toxic vapours [5] and they are clear enough to permit good optical read-out. The components are also available in a fairly constant composition. Properties of two mixtures are presented in *Table V,* which also includes the properties of a suitable single-component lacquer for comparison.

A minor problem that arises during the photolysis of DMPA is that coloured photoproducts can be formed. These give a yellowish tint to thick polymer layers. This yellowing is to some extent reversible: it decreases slightly in the dark and returns again in the light. In some mixtures the discolouration can also be seen in thin layers like those used for video discs. Although the playing of a disc is in no way affected by this discolouration (the discs are read out by red light), it looks slightly less attractive. The yellow discolouration can be avoided by using a different photo-initiator, but unfortunately this photo-initiator is less efficient.

The investigation of mixtures showed that the desired combination of properties can be obtained by using an approximate mix of components. Under the usual conditions, the mixtures mentioned here polymerize faster than the individual components investigated previously (Tables II and V).

The search for the right single-component lacquer

From the acrylates available we first made a selection based on the possible degrees of conversion and cross-linking, which determine the dimensional stability and hardness of the polymer. For a further selection we took the polymerization rate as the criterion. We continued to pay attention to aspects such as viscosity, availability, purity and price of the monomers, of course.

Selection based on degrees of conversion and cross-linking

Monoacrylates are not suitable for a single-component lacquer, because they have only one C = C bond per monomer molecule and therefore give far too little cross-linking. Polymers of monoacrylates are generally therefore soft and rubbery.

During the polymerization of di-, tri- and tetra-acrylates not all the C = C bonds are equally reactive. If one of the C = C bonds of a monomer molecule is included in a chain, the mobility of the other is greatly reduced. When more and more monomer molecules become attached to the network by one 'arm', the chance of all the C = C bonds being converted decreases rapidly. Nevertheless, an unconverted C = C bond remains a centre of high chemical reactivity. A high degree of conversion is therefore essential if a stable product is to be obtained.

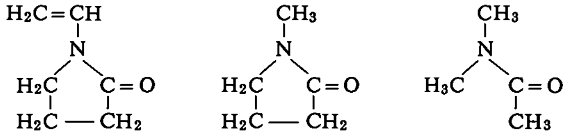
To define the region more precisely, we have correlated the degree of conversion of various acrylate monomers with the achievable degree of cross-linking, the concentration (mol/l) of the cross-links. Besides its dependence on the degree of conversion, the degree of cross-linking also depends on the molar volume of the monomer and on the details of the reaction mechanism, such as ring and ladder formation. To a first

Table III. Properties of some two-component mixtures with TPGDA as main component [a].

Second component	Viscosity at 23 °C (mPa.s)	Relative reactivity [b]	Indentation depth [c] (µm)
vinyl acetate	4.5	3.33	3.7
2-ethylhexyl acrylate (EHA)	7.1	2.14	>10
butoxyethyl acrylate	7.6	3.33	—
t-butyl cyclohexyl acrylate	11.7	1.28	7.3
phenylpropyl acrylate	10.0	1.50	9.3
ethoxyphenyl acrylate	16.2	3.07	>10
trimethylolpropane triacrylate (TMPTA) [d]	13.0	3.24	3.2
VPS - 2051 (Degussa) [e]	13.5	3.60	2.8
VPS - 2052 (Degussa) [e]	13.5	2.86	2.7

[a] 96% monomer mixture + 4% photo-initiator, exposed with TL05 lamp. The mixture contains 80% of TPGDA and 20% of the second component, except in the last three cases, where an 80/20 mixture would have too high a viscosity.
[b] See Table II, under [b].
[c] See Table II, under [c].
[d] 15% instead of 20%.
[e] 17.5% instead of 20%.

Table IV. Properties of a TPGDA/TMPTA mixture [a] after addition of N-vinylpyrrolidone (NVP), N-methylpyrrolidone (NMP) and dimethyl acetamide (DMA) with the following structures:



NVP NMP DMA

Addition [b]	Viscosity at 23 °C (mPa.s)	Relative reactivity [c]
—	13.0	3.24
NVP	7.8	6.68
NMP	10.7	4.29
DMA	6.9	2.70

[a] 96% monomer mixture + 4% photo-initiator, exposed with TL05 lamp. Without addition the mixture contains 85% of TPGDA and 15% of TMPTA.
[b] 25% of the TPGDA is replaced.
[c] See Table II, under [b].

Table V. Properties of lacquers that will give good video discs.

Lacquer	Composition		Viscosity at 23 °C (mPa.s)	Relative reactivity [a]	Indentation depth [b] (µm)
A	57% TPGDA 10% TMPTA	29% NVP 4% DMPA	7.8	6.68	1.9
B	61% TPGDA 17.5% TMPTA	17.5% NVP 4% DMPA	12.3	5.99	1.9
C	96% HDDA	4% DMPA	6.7	2.98	2.8

[a] See Table II, under [b].
[b] See Table II, under [c].

approximation, the degree of cross-linking N for a completely converted monomer is equal to

$$N = 1000\,(f-2)\,\varrho/2M,$$

where f is the functionality, ϱ the density (kg/l) and M the molecular weight (g/mol) of the monomer. For the monomers of interest to us the maximum value of N is mainly determined by M: whereas ϱ is always between 1.1 and 1.2 kg/l, M can vary by a factor of 3 to 4. Since ϱ is usually not known exactly, we shall henceforth consider not N but N/ϱ (mol/kg) as a function of the degree of conversion.

The approach to the maximum value of N/ϱ depends on the reactivity of the 'free' C=C bonds (r_1) and on that of the 'dangling' C=C bonds (r_2). In *fig. 6* the value of N/ϱ for a diacrylate is plotted as a function of the degree of conversion x for three special cases. When r_1 is very much greater than r_2, all the monomer molecules first react with one C=C bond and only then do the 'dangling' C=C bonds enter into the picture so that cross-links are formed. If r_1, on the other hand, is very much smaller than r_2, then each molecule that has reacted with one C=C bond will immediately react again with its other C=C bond. If r_1 and r_2 are of equal magnitude, the quantity N/ϱ will increase as the square of x. Because of the reduced mobility after the reaction of the first C=C bond, we would expect that in practice the curve of N/ϱ against x would lie between the lower two curves.

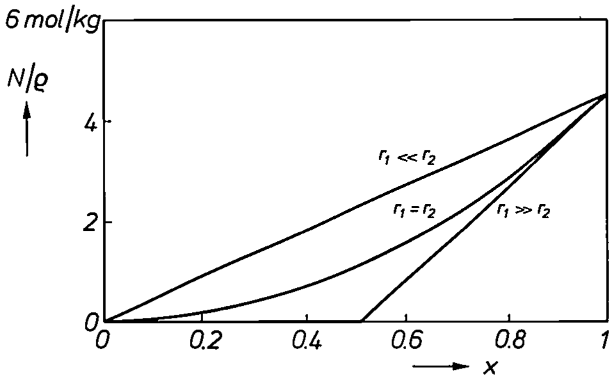


Fig. 6. Theoretical ratio of the degree of cross-linking N to the density ϱ, plotted against the degree of conversion x of a diacrylate, for different relative reactivities of the 'free' C=C bonds (r_1) and the 'dangling' C=C bonds (r_2).

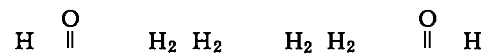
The actual reactivity ratio r_1/r_2 is not only unknown but may also depend on x. Unfortunately we are not yet able to monitor the development of the

---

[5] All acrylate monomers are toxic. Differences in toxicity are primarily determined by differences in volatility. During the manufacture of the video discs the vapours are of course exhausted, so that the production personnel are not exposed to harmful concentrations.

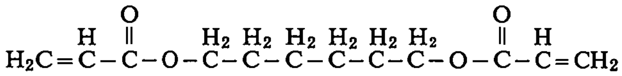
cross-linking with the reaction time, nor is it yet possible to give any reasonably well-founded statistical description of the process [6]. Nevertheless, to obtain a simple comparison of various monomers, we always assume that r_1 is very much greater than r_2, so that the lower curve is followed. For the tri- and tetra-acrylates we assume that the reactivities of the third and fourth double bond are approximately equal to r_2 and are thus very much smaller than r_1. *Fig. 7* shows the variation of N/ϱ with x for two di(meth)acrylates (one with a large molar volume and the other with a small molar volume), two tri(meth)acrylates (again with large and small molar volumes) and a tetra-acrylate. The curves indicate that with tri- and tetra-acrylates it should in theory be possible to obtain a substantially higher value of N/ϱ than with diacrylates. This is not so in practice, however. We see this, for example, if we indicate on the curves the points based on the measurements of x taken from the literature [7]. Both at 30 °C and at 50 °C a higher value of N/ϱ can be obtained with diacrylates, because x can become much higher. For the tri- and tetra-acrylates the value of N/ϱ does not become higher unless the temperature is gradually raised from 30 °C to 250 °C during the reaction, but obviously this condition cannot be applied to the manufacture of video discs.

The conclusion to be drawn is that it is preferable to start with a diacrylate. To define the choice more closely, *fig. 8* gives a plot of N/ϱ against x for a number of diacrylates. For clarity, only the theoretical values of N/ϱ associated with the measured values of x are shown [7]. At the highest temperature diethylene glycol diacrylate (DEGDA) is superior. This compound has a long flexible connection between the acrylate groups:



$$H_2C=\overset{H}{C}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-O-\overset{\overset{O}{\|}}{C}-\overset{H}{C}=CH_2$$

The flexibility is mainly attributable to the $\overset{H_2}{C}-O-\overset{H_2}{C}$ fragment. This is because the energy barrier for rotation about $O-\overset{H_2}{C}$ bonds is much smaller than for rotation about $\overset{H_2}{C}-\overset{H_2}{C}$ bonds, where the hydrogen atoms tend to obstruct one another. A good second choice is 1,6-hexanediol diacrylate (HDDA), which has a somewhat longer but slightly less flexible connection:



$$H_2C=\overset{H}{C}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-O-\overset{\overset{O}{\|}}{C}-\overset{H}{C}=CH_2$$

At 30 °C HDDA has the highest degree of cross-linking. Another candidate indicated in fig. 8 is tetraethylene glycol diacrylate (TEGDA), which has the highest degree of conversion at 30 °C.

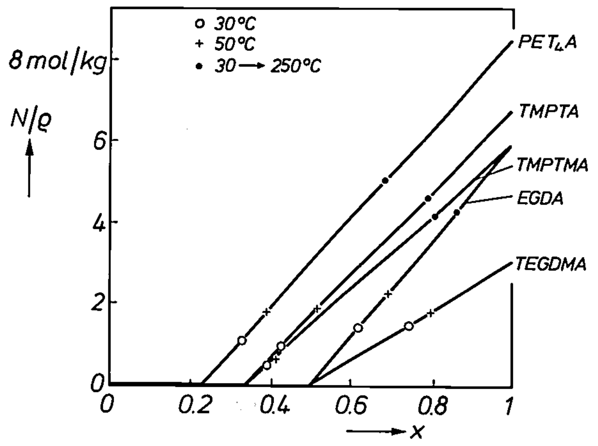


Fig. 7. N/ϱ plotted against x for some di-, tri- and tetra(meth)acrylates, i.e. tetraethylene glycol dimethacrylate (TEGDMA), ethylene glycol diacrylate (EGDA), trimethylol propane trimethacrylate (TMPTMA), trimethylol propane triacrylate (TMPTA) and pentaerythritol tetra-acrylate (PET$_4$A). The points on the curves relate to measurements of x reported in the literature at 30 °C, 50 °C and for a thermal scan from 30 to 250 °C.

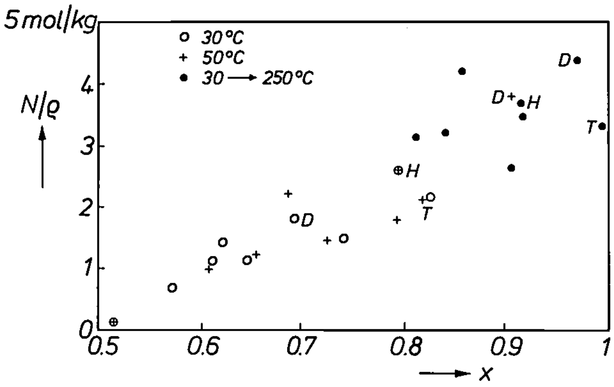


Fig. 8. N/ϱ plotted against x for a number of diacrylates. The various points were obtained in the same way as those in fig. 7. The points for di-ethylene glycol diacrylate (DEGDA), hexanediol diacrylate (HDDA) and tetraethylene glycol diacrylate (TEGDA) are denoted by D, H and T, respectively.

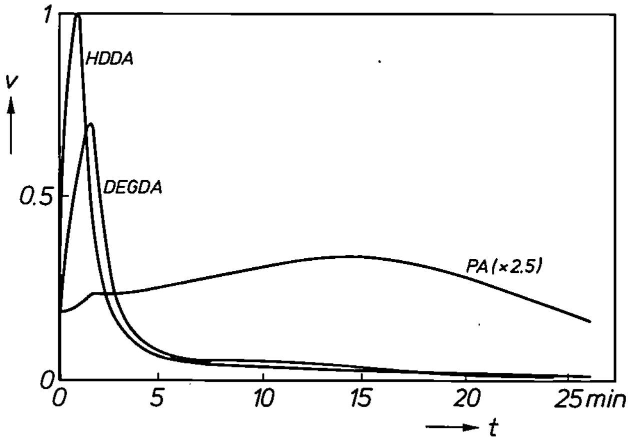


Fig. 9. Conversion rate v (in relative units) as a function of time t, for the polymerization of DEGDA, HDDA and *n*-propyl acrylate (PA).

Selection based on polymerization rate

As a consequence of the auto-acceleration the polymerization rate cannot be expressed by means of one or more rate constants, because both the propagation-rate constant and the termination-rate constant depend closely on the degree of conversion. These constants can only be determined in a dilute solution at a low degree of conversion, so that the polymer molecules formed do not 'see' each other. For our purposes such determinations are unfortunately not very useful. The reaction rates of diacrylate monomers can best be compared by determining the maximum rates. This comparison, however, is rather difficult because the reaction rate is highly sensitive to the presence of impurities, or inhibitors deliberately added to prevent spontaneous polymerization. We therefore first thoroughly purified the diacrylates selected for our experiments. To make careful measurements and comparisons of the maximum rates, we let the reactions take place much more slowly than in the actual manufacture of the discs. *Fig. 9* shows the rate-time curves of DEGDA and HDDA. The maximum conversion rate of HDDA is clearly higher than that of DEGDA.

For comparison fig. 9 also gives the curve for *n*-propyl acrylate. This compound can be regarded as 'half' of HDDA: all the C = C bonds are located in separate molecules, whereas in HDDA they are arranged in pairs. This structural difference has a considerable effect on the maximum conversion rate and the shape of the curve.

We also measured the maximum conversion rate for three other diacrylates with a useful degree of conversion and cross-linking: TEGDA (fig. 8) and the related compounds triethylene glycol diacrylate (TrEGDA) and tripropylene glycol diacrylate (TPGDA). We also determined the degree of conversion at 20 °C (owing to a difference in measuring conditions the results for DEGDA, HDDA and TEGDA are unfortunately not readily comparable with those in fig. 8). In addition we investigated the purity of the five monomers. The C = C bond content was determined by a complete bromination and the result was compared with the theoretical content at a purity of 100%.

Table VI gives the results of the various measurements. If we require the maximum conversion rate to be as high as possible, with the purity closely approaching 100%, then the only remaining candidates are HDDA and TEGDA. Of the two, TEGDA has the higher degree of conversion. For the moment, however, our preference is for HDDA, not only because of its greater purity but also because of its greater availability. It is widely used, for example, in printing inks, coatings and lacquers, and is therefore widely obtainable in a reasonably pure form.

Table VI. Degree of conversion x, maximum conversion rate v_m at 20 °C and purity z of some diacrylate monomers.

Monomer	x	v_m (%/s)	z (%)
DEGDA	0.71	0.43	94
HDDA	0.70	0.56	100
TPGDA	0.75	0.53	94
TrEGDA	0.76	0.23	99
TEGDA	0.82	0.57	98

Table VII. Maximum conversion rate v_m and the time t_m taken to reach it, for three HDDA-based lacquers and for the mixtures *A* and *B* mentioned in Table V under different curing conditions. For the polymerization in air the time t_i is given during which there is no reaction owing to the inhibiting effect of oxygen.

Conditions	Nitrogen, Low initiation rate		Nitrogen, High initiation rate		Air, High initiation rate		
Lacquer	v_m (%/s)	t_m (s)	v_m (%/s)	t_m (s)	v_m (%/s)	t_m (s)	t_i (s)
HDDA, No. 1 [a]	0.06	1180	5.4	14	2.7	51	19
HDDA, No. 2 [b]	0.49	50	9.4	5	5.2	25	11
HDDA, No. 3 [c]	0.57	50	10.6	6	6.5	25	11
A			12.4	5	11.3	11	5
B			11.4	5	10.2	13	5

[a] Contains 190 ppm of *p*-benzoquinone.
[b] Contains 15 ppm of *p*-benzoquinone.
[c] Obtained after purification of No. 2; contains less than 5 ppm of *p*-benzoquinone.

Some results

Table VII gives the maximum conversion rate v_m for three HDDA-based lacquers under different curing conditions. At a low initiation rate in a nitrogen

---

[6] R. S. Whitney and W. Burchard, Makromol. Chemie 181, 869, 1980.

[7] J. E. Moore, in: S. S. Labana (ed.), Chemistry and properties of crosslinked polymers, Academic Press, New York 1977, p. 535.

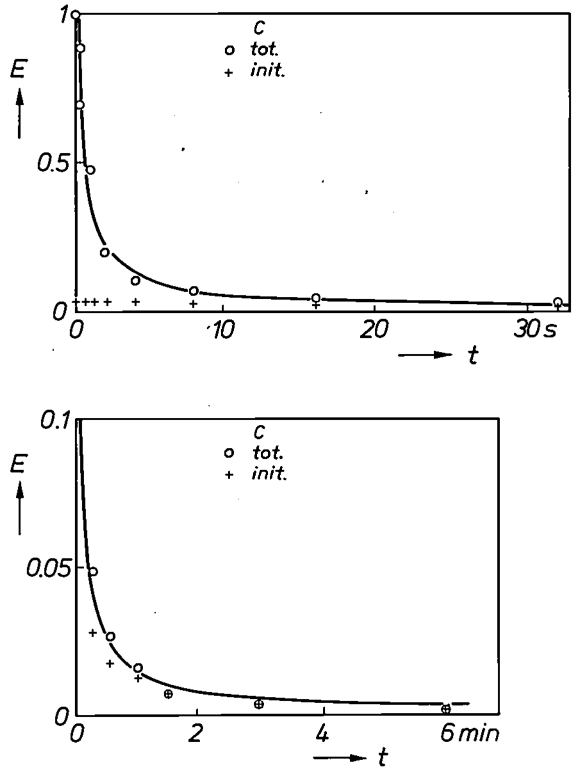


Fig. 10. Extraction curve of the single-component lacquer *C* consisting of HDDA and the initiator DMPA (Table V). The chromatographically determined total quantity of extracted material (*E*), expressed as the fraction of the initial weight of the lacquer, is plotted as a function of the exposure time *t*. The proportion of the initiator is indicated separately. Conditions: nitrogen atmosphere, four TL09 lamps, intensity at sample position 1.5 mW/cm^2.

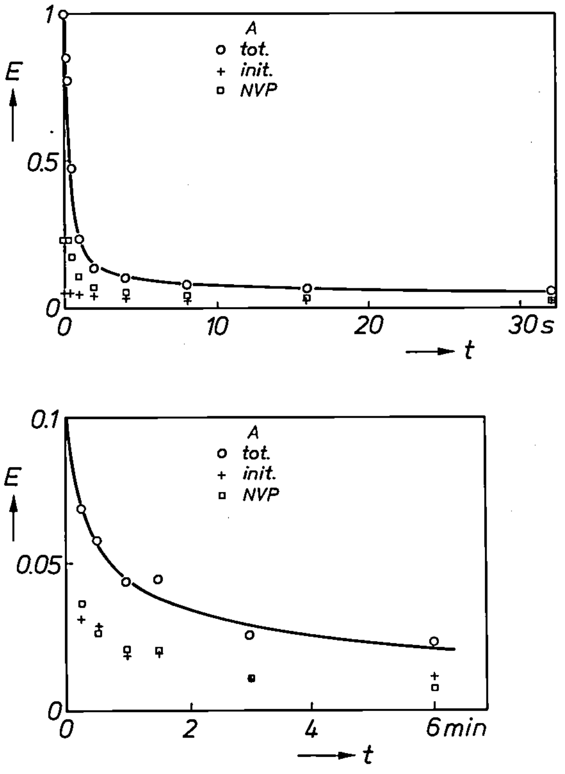


Fig. 11. Extraction curve (as in fig. 10) of the lacquer *A* consisting of a mixture of TPGDA, TMPTA, NVP and the initiator DMPA (Table V). The proportions of the initiator and NVP are indicated separately. The irradiation intensity at the sample position is 1.2 mW/cm^2.

Table VIII. Some data on the separation of LaserVision discs from a mould, measured at a pulling rate of 500 mm/min, when mixtures *A* and *B* and the single-component lacquer *C* are used.

Lacquer	Total separation energy (J)	Deformation energy of the substrate (J)	Separation energy of lacquer (J)	Separation time (s)	Maximum pulling force (N)
A	1.27	0.39	0.88	4.2	51
B	0.75	0.27	0.48	3.6	48
C	0.30	0.08	0.22	2.4	31

atmosphere, v_{m} is closely dependent on the content of the inhibitor *p*-benzoquinone in the lacquer. This compound has a retarding effect, even in the absence of oxygen. If the initiation rate is increased by a factor of 200, the variation in v_{m} with inhibitor content decreases considerably.

At a relatively low intensity of incident light (0.2 mW/cm^2) these samples do not cure well in air. The photochemical consumption of dissolved oxygen cannot apparently compete with the replenishment of oxygen by diffusion. The video discs are also manufactured in a normal atmosphere, but since the lacquer layer is enclosed between mould and substrate, oxygen cannot affect the lacquer [8]. We simulated this situation by exposing the samples and the calorimeter to a flow of air, and then covering the samples with a thin film of mylar, which is transparent to ultraviolet radiation. The polymerization was successful, but there was inhibition, particularly in the sample with the most *p*-benzoquinone.

We also performed the same experiments on the mixtures *A* and *B* listed in Table V. In a nitrogen

---

[8] Some inhibition does occur at the edge, of course. The incompletely cured edge is removed later.

atmosphere there is little difference compared with the purest HDDA lacquer, but the inhibition on saturation with air is clearly reduced. This is mainly due to the presence of NVP. In separate experiments with mixtures of HDDA and NVP it was found that the influence of NVP depends on the presence of oxygen. In a nitrogen atmosphere a mixture of HDDA and NVP polymerizes more slowly than HDDA, but this order is reversed on saturation with air.

Another subject of investigation related to the small molecules still present in a fully cured lacquer. To obtain sufficient light absorption it is customary to use a surplus of initiator, so that in addition to unconverted monomer some photosensitive initiator remains, possibly accompanied by small quantities of its photoproducts. This may lead not only to the discolouration mentioned above, but also to an undesired continuation of the photochemical processes. Small molecules may also drift slowly to the surface where, if they are hygroscopic or chemically reactive, they may adversely affect the quality of the mirror coating. It therefore seems likely that a dense network offering little scope for transport will give a more durable disc.

To obtain some idea of the quantity and mobility of the small molecules in a polymerized lacquer, we determined the 'extraction' curves by liquid chromatography. The curve for lacquer *C* with HDDA (Table V) shows that with increasing exposure time the amount of extracted material rapidly decreases, see *fig. 10.* After some time little but initiator is extracted. *Fig. 11* shows that the extract of the NVP-rich mixture *A* contains (apart from initiator) mainly NVP, which is less rapidly incorporated in the network, since it has one double bond. After a few minutes some stabilization occurs, and the quantity of extracted material hardly decreases at all with exposure time.

Good video discs can also be made with HDDA. After curing and metallization, the LaserVision pattern is indistinguishable from the pattern shown in the lower photograph in fig. 4. The lacquer is easily released from the mould. The energy required for releasing the disc plus lacquer from the mould (the total separation energy) is considerably lower than for the mixtures *A* and *B*; see *Table VIII.* This helps to prolong the life of the mould.

Since there is some warping of the disc during its separation from the mould, part of the separation energy must be attributed to the elastic deformation of the disc, so that the actual adhesion energy between lacquer and mould is lower than the total separation energy. The adhesion energies appear to be approximately proportional to the total separation energies.

Finally, we should mention that the video discs made with the mixtures and with HDDA satisfactorily pass all the normal acceptance tests.

Summary. Photopolymerizable lacquers for the manufacture of LaserVision video discs contain acrylate monomers and a photoinitiator that triggers the polymerization of the monomers on exposure to ultraviolet light. Two approaches were adopted to obtain lacquers that meet the many exacting requirements of LaserVision. In one approach a search was made for a mixture of monomers that would collectively provide the desired properties. In the other an effort was made to find a monomer that itself had all the desired properties. Both approaches led to the desired result: lacquers that give good LaserVision discs.