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The use of Langmuir–Blodgett films as recording layers in optical information carriers

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ABSTRACT. The review deals with methods of recording and reproducing information for external computer memory devices in which Langmuir–Blodgett films are used as carriers and also with the physical effects occurring in these films, which may be used in the future for the creation of new superdense optical information carriers. Attention has concentrated on the photochromic reactions in the *J*-aggregates of Langmuir–Blodgett films, which permit the reversible recording of information. In many cases the preparation of the carrier and the technical characteristics of the corresponding memory devices are described in detail. The review considers the original studies and patents on this topic which have been published during the last 15 years.

The bibliography includes 55 references.

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I. Introduction

The problem of creating information carriers for optical reversible memory devices (MD) on computers as well as improvement of the density of the recording in such devices are of extremely great current interest. The optical memory devices of the archive type widely used nowadays do not provide for the local deletion and re-recording of information. The first reversible optical memory devices which became commercially available are memory devices with thermomagnetic recording and magnetooptical reproduction based on the Kerr and Faraday effects[1].

Numerous procedures for the recording and reproduction of information based on new principles as well as information carriers with recording layers having a wide variety of compositions, in particular with film recording layers prepared by the Langmuir–Blodgett method[2], have been proposed recently.

The Langmuir–Blodgett films (LB films) consist of layers of amphiphilic molecules (i.e. molecules having hydrophilic and hydrophobic components), which are ordered at the molecular level. They are transferred successively from the surface of a liquid subphase onto a solid support.[3]

The apparatus for the preparation of LB films is illustrated in Fig. 1. The process involving the deposition of a LB film begins with the deposition onto the surface of a liquid which is a solution of an amphiphilic substance in a volatile inert solvent at a concentration of the order of 0.1%. After the solvent has been evaporated, a monomolecular film consisting of molecules oriented uniformly with respect to their hydrophilic and hydrophobic groups in relation to the surface of the liquid is produced. The film is then removed by a mobile barrier, whilst monitoring the surface tension.

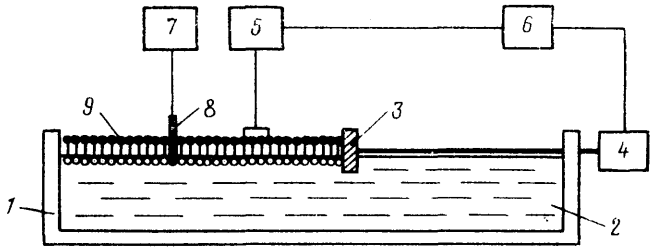


Figure 1. Schematic illustration of the apparatus for the deposition of Langmuir–Blodgett films on a solid support: *1*, bath; *2*, doubly distilled water; *3*, mobile barrier; *4*, motor driving the barrier for the compression of the monomolecular film; *5*, balance for the measurement of surface pressure; *6*, feedback device for monitoring the surface pressure; *7*, system for the lowering of the support; *8*, support; *9*, LB film.

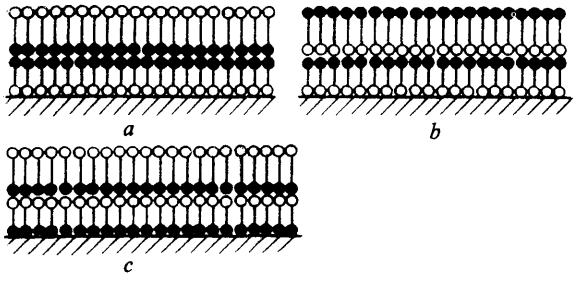


Figure 2. The structures of the Y-type (*a*), X-type (*b*), and Z-type (*c*) LB films

After the attainment of a certain film surface area, a sharp break appears on the plot of the surface pressure against the area per molecule, indicating the formation of a close-packed monolayer.

At the break point or at a somewhat lower surface pressure, the support is passed through the film and the amphiphilic molecules are deposited on the support with retention of their packing and orientation. If the support is hydrophobic, then the first layer of molecules is oriented with the hydrophobic ends towards the support and if it is hydrophilic the reverse orientation occurs. By repeating successively the procedure described, it is possible to deposit up to several hundred monolayers on the support. Depending on the deposition conditions, it is possible to obtain centrosymmetrical LB films of the Y type (Fig. 2*a*) with the opposite orientation of the molecules in neighbouring layers, or non-centrosymmetrical LB films of the X type (the hydrophobic ends of the molecules adjoin the support) (Fig. 2*b*), or such layers of the Z type (the hydrophilic ends adjoin the support) (Fig. 2*c*).

The constantly growing interest in the applications of LB films in a wide variety of engineering fields such as molecular electronics[4–7], optoelectronics[8–11], gas sensors[12–14], as lubricants for magnetic memory devices[15], in molecular engineering[16–18], etc. can be explained by a whole series of their unique properties such as an accurately specified thickness, which can be controlled to within a few angstroms, a high degree of homogeneity, and a constant mutual orientation of the molecules and their functional groups. It is then possible to create assemblies of molecular layers and individual molecules of any architecture.

The possibility of controlling the orientation of the molecules and the interaction between them at rigorously controlled distances makes it possible to achieve a reversible optical memory in LB films. The recording processes in such films can be of two types — chemical and orientational. The former are divided into intramolecular transformations (for example *cis–trans* isomerisation[19]) and chemical reactions of neighbouring molecules in one monolayer (for example, dimerisation[20] and polymerisation[21]) and in neighbouring monolayers, while the latter can be divided into *J*-aggregation processes[22,23] (i.e. rearrangements of an elementary two-dimensional cell of the LB film), degradations of *J*-aggregates[24,25], the reversible phase transitions of various kinds, including those involving the appearance of photodichroism under the influence of polarised light[26].

The recording processes based on chemical reactions make it possible to achieve a satisfactory permanence of the information and a high signal/noise ratio in the corresponding memory devices, but here it is difficult to achieve a reversible recording. Recording layers based on spiropyrans, in which a reversible structural rearrangement under the influence of UV and visible radiation can be readily achieved, are an exception[27].

The greatest stability of the recording layer can be attained if it is subjected to preliminary polymerisation by irradiation with UV light or low-energy electrons, which can be done also without the degradation of the LB film[28–31]. Information can be recorded in such layers also by means of the degradation of the polymer.

In recent years attempts have been made to create multilayer polyimide LB films which are thermally stable up to 700 K. These will be the most thermally stable thin organic films among those known to date.

With the aid of photochemical recording, it is possible to ensure also the replication of recorded information. Thus the photodimers formed in LB films under the influence of optical radiation have both optical and physicochemical properties different from those of the individual molecules. When the mixed layer is deposited by the Langmuir–Blodgett method onto a monolayer which has already been modified, the dimers are arranged on dimers and individual molecules are arranged on individual molecules. Thus the subsequent layer replicates the information recorded on the preceding layer. The upper layer can be separated from the lower layer by placing on its surface a film of poly(vinyl alcohol) and then splitting off both films[32,33]

The recording processes based on changes in the orientation and the relative positions of the molecules in the LB film make it possible to achieve the reversible recording of information, but the corresponding memory devices cannot at present compete with magnetooptical memory devices as regards the permanence of the recording, the signal/noise ratio, and a number of recording/re-recording cycles. Furthermore, when LB films consisting of two and more coaggregates are used (which is frequently necessary in recording procedures based on *J*-aggregation and *cis–trans* isomerisation processes), the problem of the formation of domains in the LB film owing to phase separation in the mixed monolayer arises[34]. The molecules in such island domains behave in many respects like a single assembly, as a result of which the recorded bit is blurred and the signal/noise ratio in the corresponding memory devices is therefore reduced. In an attempt to overcome these phenomena, use is made of special conditions in the deposition of films from a non-densely compressed monolayer whereupon the LB film consists of a "two-dimensional liquid" or various stabilising additives incorporated in the monolayer which diminish the size of the structured domains by becoming distributed along their boundaries.

Briefly, a vigorous search for reversible optical systems based on the LB technology and for ways of modifying thermoptically is being prosecuted at the present time, which will undoubtedly yield positive results in the future. The principal advantage of an optical memory with a carrier based on LB films over a magnetooptical memory will apparently become the achievement of multicolour recording on photochromic LB films containing either dyes of several types with absorption bands in different spectral ranges, located in successive layers, or one dye in one layer with various photochromic groups attached to one molecule, or coaggregate dyes. Multicolour optical recording makes it possible to create memory devices with a recording density several times greater than in the usual optical memory devices by recording several bits of information simultaneously at a single location of the laser spot.

The review deals with the principal methods of recording and reproducing information on carriers prepared by the Langmuir–Blodgett method proposed recently, the specific compositions and methods of depositing recording layers, as well as the physicochemical processes occurring in LB layers. There is a prospect that these processes may be used to record information. The main bulk of the review is devoted to reversible systems, while among systems of the archive type only some are mentioned.

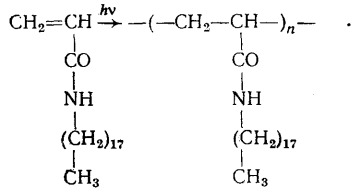
II. Archive recording

Archive memory devices do not allow the deletion and re-recording of information; they are designed for the long term storage of large amounts of information and belong to the so called "write once/read many" type in contrast to the reversible "write many/read many" memory devices. The principal requirements which must be met by archive devices is the greatest possible density of recording and the shortest possible access time to the data.

We shall consider certain physical principles on which information recording processes in these devices are based.

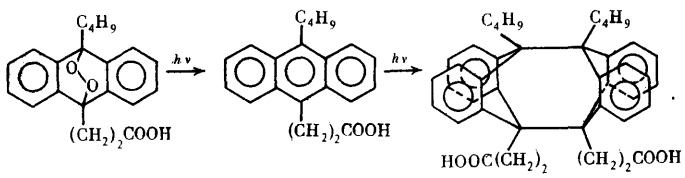
1. Photopolymerisation

Several systems have been proposed in which the local polymerisation under the influence of light is used to record information. An example of such a system has been examined in a study[21] where a stable polymer was formed under the influence of UV radiation in a LB film based on *N*-octadecylacrylamide as a result of the reaction



2. Photodimerisation

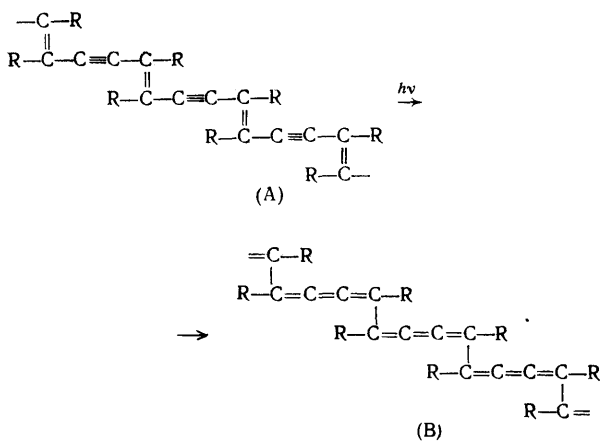
Intermolecular photodimerisation of neighbouring 9-anthryl-10-butyl-3-propanoic acid molecules has been used[20] to record information on a LB film:



This reaction proceeds in an arachidonic acid matrix with acid : matrix = 1 : 1 and 1 : 3 ratios under the influence of laser light with a wavelength of 420 ± 2.5 nm. The optical absorption spectrum of the film changes significantly under these conditions. The reverse reaction is not observed either in the dark or on irradiation with the light corresponding to the absorption band of the dimer over a period of 14 h.

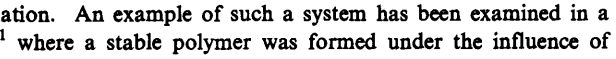
3. Photoinduced transformation of the polymer

An optical information carrier has been described[35] in which the acetylenic form (A) of polydiacetylene is converted into the butadiene form (B) under the influence of UV radiation:



The rate of recording on such films is 10^8 bits s^{-1} and the required energy density for recording is less than 800 J m^{-2}.

The carrier is prepared as follows. The monomer, for example pentacosa-10,12-diynoic acid



is deposited on the surface of water, buffered with $CdCl_2$ (10^{-4} M, pH 6.1), at 15 ± 0.1 °C by the Langmuir–Blodgett method. Chloroform, in which the acid concentration is 0.7 kg m^{-3}, is used as the solvent. 40 Monolayers of a Y-type LB film are deposited on a sulphuric acid-treated quartz glass support at a surface pressure of 25×10^{-3} N m^{-1}. This results in the formation of a coating having a thickness of the order of 1000 Å. Under the influence of 5 W m^{-2} UV radiation (λ = 240–400 nm), the acid polymerises in 40 min. The spectrum of the polymer then corresponds to the (A) form [Fig. 3, curve (*A*)]. On further irradiation with UV light up to a total dose of 100 J m^{-2}, the absorption spectrum changes [Fig. 3, curve (*B*)], indicates the conversion of the polymer into the (B) form. The recording of information is thus achieved. The change in the relative amounts of the polymers in the (A) and (B) forms as a function of the absorbed energy is illustrated in Fig. 4. The shorter the irradiation wavelength, the higher the efficiency of the (A)→(B) transformation.

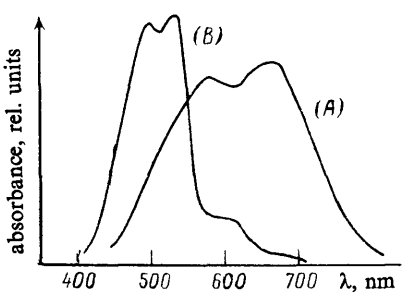


Figure 3. Absorption spectrum of a polydiacetylene LB film in the acetylene (A) and butadiene (B) forms.

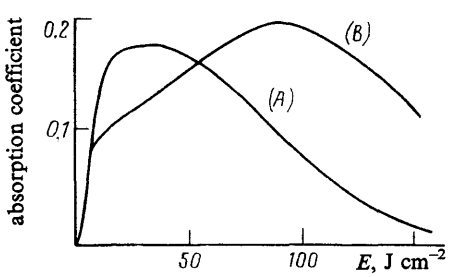


Figure 4. Variation of the relative amount of polyacetylene in the acetylene (A) (λ = 638 nm) and butadiene (B) (λ = 535 nm) forms as a function of the absorbed energy.

Archive devices with a carrier based on a LB film cannot as yet compete with the traditional optical discs, on which information is recorded by the photolithographic method, despite the simple

recording technology and the higher information density. The principal disadvantages of the recording procedures described above are the long photopolymerisation reaction and phototransformation times as well as the inadequate lifetime of the recorded information. Nevertheless studies are being conducted in order to reduce the photochemical reaction time in such systems[36] and also in order to stabilise the reaction products with the aid of different kinds of coaggregates.

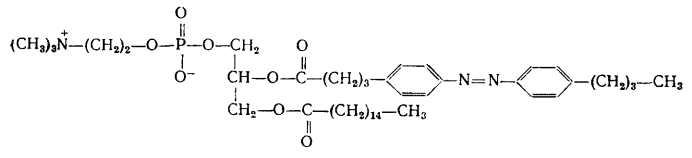
III. Reversible recording

The reversible methods for the recording of information are designed for external computer memory devices in which it is necessary to be able to delete the previously recorded information and to record new information. The principal requirements which must be met by such devices is the attainment of the largest possible number of recording–re-recording cycles as well as the greatest possible permanence of the recorded data. Reversible memory devices are divided into locally reversible, in which it is possible to re-record selectively over part of the existing information on the carrier, and others in which information can be re-recorded only after deleting the previously recorded information from the entire carrier. As regards the locally reversible memory devices, the latter are used widely at the present time with the information carrier in the form of magnetic discs with a realistically attainable recording density of 10^{10} bits m^{-2} as well as magnetooptical devices already prepared for mass production[1] with a recording density reaching 10^{12} bits m^{-2}.

1. Reversible recording without local re-recording

(a) *Cis–trans* isomerisation

LB films of photochromic phopholipids containing azobenzene have been investigated[19], for example:



When they are irradiated with UV light, *cis–trans* isomerisation (of azobenzene) takes place, the *cis*-isomer predominating in the film; on irradiation with visible light (at the wavelength λ = 540 nm), the *trans*-isomer predominates. The refractive index of the film then changes. By recording the modulation of the refractive index, it is possible to reproduce the recorded information. However, thermal equalisation of the relative amounts of the *cis*- and *trans*-isomers as a result of the reverse reaction is observed in this system, so that the proposed carrier is as yet difficult to use in memory devices.

It has been suggested that photochromic reactions, i.e. reactions involving a reversible change in the structure of molecules or in their electronic state under the influence of light accompanied by a change in the colour of the substance, have been proposed for the optical recording of information. This also entails as a rule a change in the refractive index of the film. Photochromic materials comprise a broad class of compounds—spiropyrans, metal dithizonates and metal-phthalocyanines, polycyclic hydrocarbons, etc. Since photochromic materials do not form a stable LB film, they are introduced into a matrix consisting of the film-forming substance, which is usually an aliphatic acid containing between 10 and 25 atoms together with stabilising additives. Sometimes the resulting film is also polymerised.

A large class of optical carriers, prepared by the Langmuir–Blodgett method and capable of the undergoing *cis–trans* isomerisation under the influence of light, has been described[37]. It includes photochromic materials with a N=N bond (azobenzene derivatives) or a C=C bond (indigo and thioindigo derivatives into which a hydrocarbon group, such as alkyl, alkoxy-, alkylacyl, or alkylamino-groups containing at least 10 and preferably 14–25 carbon atoms, has been introduced). We shall now list some of these compounds; for example, we have 4-monostearylamino-azobenzene, *N,N'*-distearylindigo, 5-octadecyl-5'-t-butylthioindigo, and 5-octadecyl-1,8-naphthylthioindigo. Aliphatic acids and their derivatives (stearic and arachidonic acids, methyl stearate, stearyl alcohol), tripalmitin, phospholipids etc. can be used as the film forming components necessary for the formation of the LB film. The molar ratio of the film forming component to the photochromic substance is varied from 1:1 to 6:1, the 1:1 and 2:1 ratios being most preferred. The solvents employed are benzene, chloroform, n-hexane, cyclohexane, and ethyl ether. The concentrations of the photochromic and film-forming substances in these solvents vary from 0.1 to 10 g m^{-3} (concentrations in the range 0.1–1 g m^{-3} being most preferred). The aqueous subphase is buffered by barium, calcium, or lithium salts at concentrations in the range 10^{-3}–10^{-5} M (pH 4–9). Acrylic resin is deposited on the recording layer in order to improve the operating characteristics of the carrier.

Several patented carriers will be examined below as specific examples[37].

Example 1. One of two mixtures—10^{-3} M solution of 4-monostearylaminoazobenzene in toluene or 10^{-3} M solution of a mixture of monostearylaminoazobenzene and stearic acid (in molar proportions of 1:2) in benzene—is irradiated with light at a wavelength of 360 nm. The irradiated solution (2.5×10^{-7} m^3) is deposited on water (pH 7, T = 18 °C) and the resulting film is compressed at a rate of 10 mm min^{-1} to the surface pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}. After that, 30 monolayers of the film (750 Å) are deposited in succession on the support by the LB method. Information is recorded by means of a laser beam at a wavelength of 440 nm, focussed to a diameter of 1 μm. Before recording, the medium absorbs at a wavelength of 440 nm, while after recording it is transparent in this region. Information is retained for a fairly long time (for 30 days in the case of the carrier prepared from 4-monostearylaminobenzene and stearic acid).

Example 2. One of two mixtures—10^{-3} M *N,N'*-distearylindigo (the method of preparation has been described in a patent) in benzene or 1.5×10^{-3} M solution of a mixture of *N,N'*-distearylindigo and tripalmitin (molar ratio 1:2) in benzene—is irrigated with light at λ = 580 nm. The irradiated solution (2×10^{-7} m^3) is deposited on water (pH 5.8; T - 18 °C) and the resulting film is compressed at a rate of 1.6×10^{-4} m s^{-1} to the surface pressure $P_0 = 25 \times 10^{-3}$ M m^{-1}. Next, 20 monolayers of the film are deposited by the LB method on a hydrophobic glass carrier (treated in cadmium arachidate) by the LB method. The recording is performed with a laser at a wavelength of 440 nm. Before recording, the medium is transparent in the region of 540 nm, but after irradiation it becomes absorbing. The absorption spectra of the carrier containing *N',N'*-distearylindigo and tripalmitin, before and after recording, are illustrated in Fig. 5.

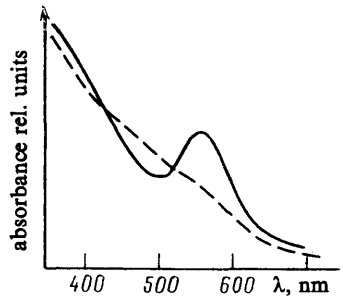
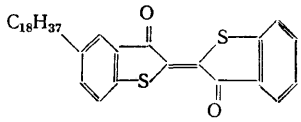


Figure 5. Absorption spectra of a carrier containing *N,N'*-distearylindigo and tripalmitin before recording (dashed line) and after recording (continuous line) with a laser operating at a wavelength of 440 nm.

Example 3. A solution of 5-octadecylthioindigo (10^{-3} M) (the method of preparation has been described in a patent[37]), i.e.



in benzene is irrigated with light at λ = 560 nm. The irradiated solution (3×10^{-7} m^3) is deposited on the surface of water (pH 5.2; T = 18 °C) and the resulting film is compressed at a rate of 1.6×10^{-4} m s^{-1} to the surface pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}. Next, 20 monolayers are deposited on a hydrophobic glass support (treated with cadmium arachidate) by the LB method. The recording is carried out at a wavelength of 560 nm. The absorption spectra before and after irradiation are presented in Fig. 6.

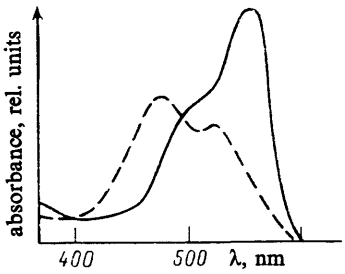
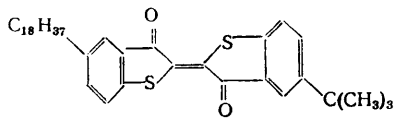


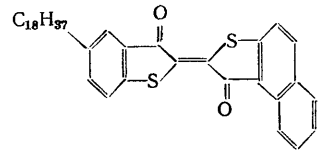
Figure 6. Absorption spectra of a carrier based on 5-octadecylthioindigo before recording (dashed line) and after recording (continuous line) at a wavelength of 560 nm.

Example 4. A solution of a mixture of 5'-t-butyl-5-octadecylthioindigo (0.5×10^{-3} M) i.e.



and tripalmitin (molar ratio 1:2) in chloroform is irradiated with light at a wavelength of 550 nm and 20 monolayers of the film are deposited on a chromium-plated support treated with cadmium arachidate. The recording is carried out a wavelength of 450 nm. The medium is transparent at a wavelength of 450 nm before recording and absorbs in this region after recording.

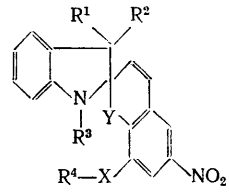
Example 5. A solution of 5-octadecyl-1,8-naphthalthioindigo (0.5×10^{-3} M), i.e.



and tripalmitin (molar ratio 1:2) is irradiated with light at a wavelength of 600 nm and 30 monolayers of the film deposited by the LB method on a glass support treated with cadmium arachidate. The recording is performed at a wavelength of 480 nm. Before irradiation, the medium absorbs in the region of 480 nm and after irradiation it is transparent in this region.

(b) Photochemical reactions in *J*-aggregates of organic dyes

The optical carriers described in patents[38–40] contain *J*-aggregates of spiropyrans of the type



where R^1 and R^2 are long alkyl group, R^3 is an alkyl group containing at least 10 and preferably 14–24 carbon atoms (hexadecyl, octadecyl, etc.), X is a single bond or one of the groups $-C_nH_{2n}OCO-$, $-C_nH_{2n}COO-$, $-C_nH_{2n}NHCO-$, $-C_nH_{2n}-CONH-$, or $-C_nH_{2n}O-$, where $n \geqslant 0$ (the $-CH_2OCO-$ or $-O-$ groups are most preferred), R^4 is an alkyl group containing at least one carbon atom, and Y=O or S. Among spiropyrans, the following are more preferred: 8-methoxy-3,3'-dimethyl-6-nitro-1'-octadecyl[2*H*-1-benzopyra-2,2'-indoline] and 8-dodecasonyloxy-3,3'-dimethyl-6-nitro-1'-octadecylspiro[2*H*-1-benzopyran-2,2'-indoline].

These spiropyrans, deposited on a carrier by the LB method, give rise to *J*-aggregates on heating[27,41–43]. The aggregates have narrower absorption bands than the unreacted dye, which makes it possible to increase the sensitivity of the method. The absorption bands undergo a bathochromic shift on formation of the *J*-aggregates.

The carrier can consist of dyes of two and more types[39]. Information is then recorded by means of laser beams at different wavelengths focussed in one spot.

On exposure to UV radiation, the spiropyrans photomerise to the corresponding photomerocyanines having maximum absorption peaks in the range 400–700 nm. However, these photomerocyanines are unstable and are usually reconverted into the initial spiropyrans even in the dark. On the other hand, if the

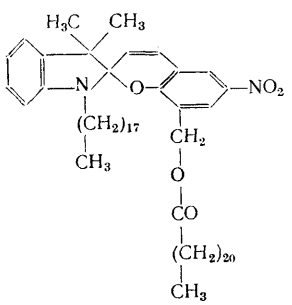
photomerocyanines are converted into *J*-aggregates as a result of a thermal reaction, the latter become more sensitive.

Aliphatic acids or their salts with polar groups are used to stabilise photomerocyanines in a LB film. One should use preferably acids with 14–24 carbon atoms (myristic, pentadecanoic, palmitic, heptadecanoic, stearic, nonadecanoic, behenic, etc.).

The solvents employed are chloroform, benzene, toluene tetrahydrofuran, acetonitrile, acetone, ethanol, etc. The solute concentrations are in the range 0.1–3 wt.%.

We shall now examine several specific examples.

Example 1. A solution of the spiropyran (3 M) (the method of preparation has been described in a patent[38])



and n-octadecane (in molar proportions of 1:2) is deposited on the surface of an aqueous subphase (pH 7.2; T = 18 °C). Next, 12 monolayers of a Y-type film are deposited on a hydrophobic glass [treated in a 10% (by volume) solution of chlorotrimethylsilane in toluene for 30 min] by the LB method. The absorption spectrum of the resulting film is illustrated in Fig. 7 (curve *A*). After the film has been irradiated with UV light for 10 min, a peak appears in the spectrum in the region of 583 nm, which is characteristic of photomerocyanine (curve *B*), while after heating by IR irradiation to 35–40 °C, *J*-aggregates appear (curve *C*). During the recording of information by means of a laser at a wavelength of 618 nm and an energy density of 5×10^3 J m^{-2}, there is a local reconversion of the photomerocyanine into the spiropyran (the absorption spectrum *A* is restored). Information is read by means of a laser beam with an energy density of 50 J m^{-2} and is deleted by UV light and heating. Information is not lost in the course of 5000 h and longer.

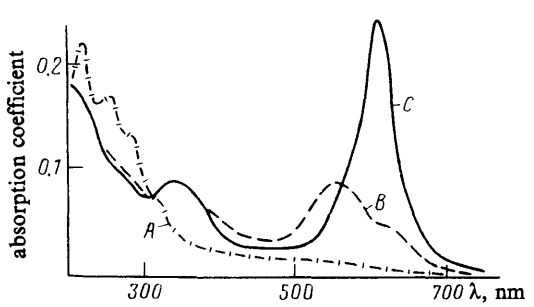
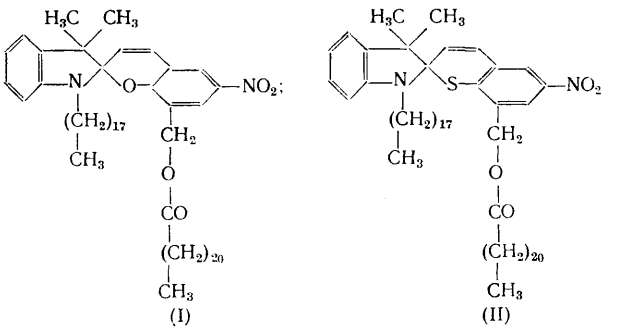


Figure 7. Absorption spectra of a LB film in a mixture of a spiropyran[39] and n-octadecane (molar ratio 1:2) before irradiation with UV light (*A*), after irradiation (*B*), and after additional heating by IR radiation to 35–40 °C (*C*). Heating results in the formation of *J*-aggregates of the corresponding photomerocyanine; (I) and (II)—dyes (see text).

It is also possible to record information by the conversion of the spiropyran into photomerocyanine[40].

Example 2. Two spiropyrans[39]



are deposited in succession on a carrier: 1 mmol of the spiropyran and 2 mmol of n-octadecane are dissolved in chloroform, 7×10^{-7} m^3 of the solution is deposited on the surface of an aqueous subphase buffered with sodium phosphate (pH 7.2; T = 18 °C), the resulting film is compressed to the pressure $P_0 = 20 \times 10^{-3}$ N m^{-1}, and 20 Y-type monolayers are deposited by the LB method on a hydrophobic glass support treated in 10% solution (by volume) of chlorotrimethylsilane in toluene for 30 min. The same procedure is gone through with the second spiropyran.

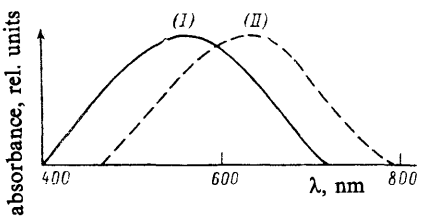


Figure 8. Absorption spectra of a carrier consisting of two spiropyrans[39] after their conversion into the corresponding photomerocyanines as a result of UV irradiation.

After this, the carrier is irradiated with the light from a UV lamp (at a wavelength of 350 nm) for 10 min. This results in the formation of photomerocyanines whose absorption spectra are illustrated in Fig. 8. (When two and more dyes are used, it is essential that their maxima should differ by at least the half-width of the absorption peak of the *J*-aggregates, i.e. by 20–30 nm.) The carrier is then heated by an IR lamp to 35–40 °C for 15 min. The spectra of the resulting *J*-aggregates are shown in Fig. 9. Evidently the peaks undergo a bathochromic shift by 35–50 nm and are narrowed to a half-width of about 30 nm.

The recording is carried out by means of two lasers operating at wavelengths of 618 and 653 nm and with an energy density of 5×10^3 J m^{-2}. Information is read by the same lasers at an intensity of 50 J m^{-2}.

Information is deleted by UV irradiation and by heating the carrier.

Yet another class of photochromic materials, whose complex molecule contains benzothiopyran, has been described[44]. A non-irradiated LB film with the photochromic substance has no absorption peaks in the range 500–900 nm, while the film irradiated with UV light absorbs strongly in the range 600–850 nm. The carrier consists of three layers—recording, refracting, and reflecting. A laser operating at a wavelength of 780 nm and with a power of 7.5 mW is used for recording. The sensitivity of the recording for a 20% change in the reflectance is 1.5×10^3 J m^{-2}. The signal/noise ratio in the reproduction of the information is 54 dB.

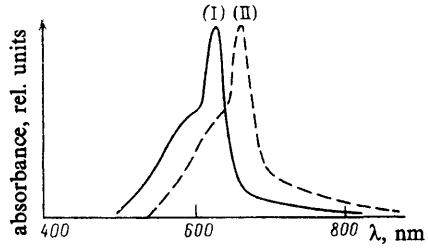
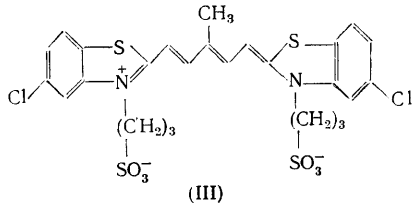
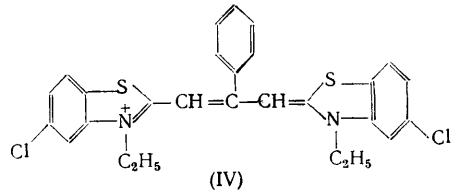


Figure 9. Spectra of photomerocyanines after the formation of *J*-aggregates; (I)–(II)—dyes (see text).

Multicolour carriers based on dyes containing *J*-aggregates have been proposed[24,45]. The following dyes are most preferred:





At least two of the following three substances are employed as the film-forming materials: dioctadecylammonium chloride (DODAC), stearylamine, and methyl stearate. It is possible to use arachidonic acid alone.

Example 1. The dye (III), stearylamine, and methyl stearate (molar ratios 1:1:3, overall concentration of stearylamine and methyl stearate 10^{-9} kg m^{-3}) in the 4:1 chloroform–methanol mixed solvent is deposited on the surface of water at 16 °C and the layer is compressed to surface pressure $P_0 = 35 \times 10^{-3}$ N m^{-1}. Next, 25 monolayers of the film (800 Å) are deposited by the LB method on a glass support coated by a layer of aluminium (2000 Å).

The recording is performed with a semiconductor laser operating at a wavelength of 780 nm, with a power of 6×10^{-3} W and with a pulse duration of 10^{-7} s. The *J*-aggregates undergo local decomposition under these conditions. The absorption spectra of such a mixture before and after recording are illustrated in Fig. 10.

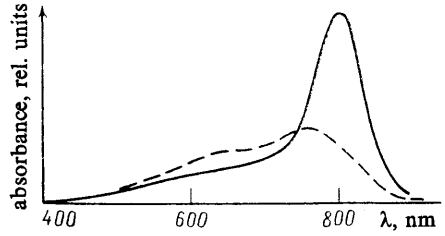


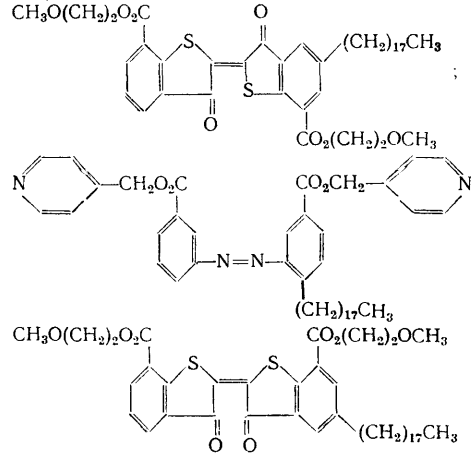
Figure 10. Absorption spectrum of the dye (III), stearylamine, and methyl stearate (molar ratio 1:1:3) in a LB film before recording (continuous line) and after recording (dashed line) with a laser operating at a wavelength of 780 nm. Irradiation results in the local decomposition of *J*-aggregates.

Example 2. A LB film of the dye (IV) and arachidonic acid (molar ratio 1:2) is deposited on top of the recording layer prepared as described in example 1. The film is compressed on the surface of water (T = 16 °C) to the surface pressure $P_0 = 30 \times 10^{-3}$ N m^{-1} and 6 monolayers of the film (200 Å) are deposited. The recording is performed with two lasers having a power of 3.5×10^{-3} W and operating at the wavelengths corresponding to the absorption peaks of the two dyes—at 670 and 780 nm.

(c) Photochemical liberation of the metal

The photochemical liberation of the metal in the LB film has been proposed in a number of studies[46–51] as reversible reaction.

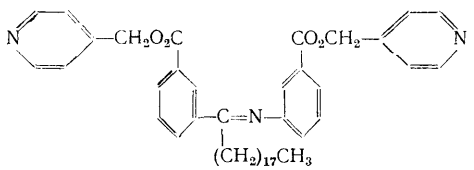
Example 1. One of the substances below[46–48], i.e.



is dissolved in $CHCl_3$ and deposited on an aqueous subphase buffered with $AgNO_3$ (pH 5.2). After the evaporation of $CHCl_3$, between 1 and 25 monolayers of the film are deposited by the LB

method on a glass support, the film being simultaneously irradiated with light at a wavelength of 450 nm. The recording is carried out with a laser operating at a wavelength of 550 nm. The absorption peak at 620 nm changes under these conditions. The reading of information is also based on this peak. Information is deleted by laser light at a wavelength of 450 nm in the course of 3 min.

Example 2. The substance



is dissolved in $CHCl_3$ and is deposited on the surface of an aqueous subphase containing Cu^+ ions (pH 5.2). After the evaporation of $CHCl_3$, between 1 and 25 monolayers of the film are deposited by the LB method on a glass support, the film being simultaneously irradiated with light at λ = 313 nm. The recording is carried out by means of a laser beam at a wavelength of 450 nm and is read from the change in the peak in the region of 530 nm in the absorption spectrum of the film. Information is deleted by irradiation with light at λ = 313 nm for 3 min[49–51].

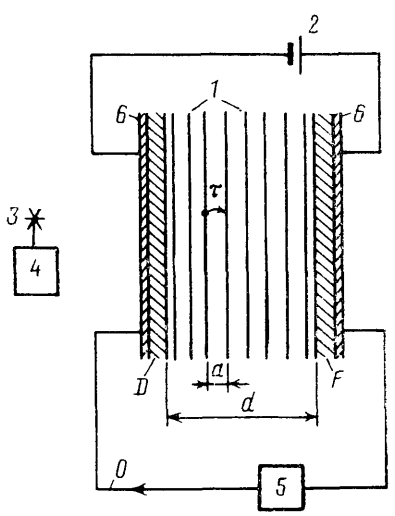


Figure 11. A multilayer carrier comprising polydiacetylene LB layers: *1*, carrier; *2*, source of supply; *3*, laser; *4*, modulator; *5*, optical amplifier; *6*, electrodes; *D*—photoinjection layer; *F*—fluorescent layer; *O*—optical loop.

In conclusion of this Section, we shall deal with a fundamentally new method of recording information on a multilayer carrier prepared by the LB technology, which can be employed in operating memory devices.

(d) Photoelectron recording on a multilayer carrier

A patent[52] describes how diacetylene LB films, polymerised to achieve stability by UV or electron irradiation, are placed between a photoinjection layer *D* and a fluorescent layer *F* (Fig. 11).

The recording is carried out with a laser fitted with a modulator. During recording, electrons are emitted from the layer *D* and are then caused by the electric field, generated in a source connected via electrodes to the carrier, to jump from layer to layer for as long as the field operates. The *F* and *D* layers can be connected by the optical loop O fitted with an optical or electrical amplifier. The loop is used to maintain the supply to the *D* layer and makes it possible to store the recorded information for a long time.

An 8-layer information carrier, possibly containing an even greater number of layers, has been described[52].

We shall consider the behaviour of an electron after its emission from the *D* layer. Suppose that τ is the time taken for the jump to the next polydiacetylene plane, whereupon

$$1/\tau = \nu \exp(-2ka),$$

where ν is the background frequency, a the distance between the layers, and $k^2 = 2mA/h^2$ (A is the electron affinity of the layer and m the mass of the electron).

If a potential $V > V(h) = n^2 k_B T/e$, where n is the number of layers, k_B the Boltzmann constant, T the absolute temperature, and e the charge of the electron, is applied to the carrier then the drift along the field exceeds the diffusion of the electron over the distance a. Under these conditions, the energy difference between the electrons in neighbouring layers is greater than $k_B T$ and the reverse jump against the field beomes unlikely. For a film made up of 8 layers at room temperature, $V(h) \simeq 0.2$ V. When $a = 10^{-9}$ m, $A = 1.6 \times 10^{-19}$ J, and $\nu = 10^{14}$ Hz, the time τ between the jumps is 8.8×10^{-6} s. Thus, when a potential of 0.2 V is applied to the carrier, the electron injected into the first layer emerges from the 8th layer after 70 μs.

The laser beam is modulated in such a way that the pulse has a width t and a period t/n. The set of light pulses corresponding, for example, to the 10011010 datum is transformed into the presence or absence of a charge in the corresponding layer after a time t. The closed optical loop *O* makes it possible to increase the storage time. It is also possible to use several layers carrying a charge q_m per bit. The criterion indicating that neighbouring bits will not diffuse into one another after N cycles as described by the expression

$$V/V(h) > N/M^2,$$

where M is the number of layers used to store one bit of information.

In reading the information, it is possible to employ the current differentiation method instead of detection with the aid of the fluorescent *F* layer. The maximum current change is $\Delta I = q_m/n\tau$.

Figs. 12 and 13 illustrate another carrier made up of polydiacetylene bilayers of two types, differing in the electron affinity by $\Delta A \simeq 10 k_B T$. For the electron jumps illustrated in the figures by arrows, we have

$1/\tau_{12}(s) = \nu \exp(-2ka) \exp(-\Delta A/k_B T)$ in a weak field $E < \Delta A/(e.a)$;

$1/\tau_{12}(l) = \nu \exp(-2ka)$ in a strong field $E \geqslant \Delta A/(e.a)$;

$$1/\tau_{11} = \nu \exp(-4ka),$$

where τ_{12} is the time taken for a jump from a type *1* layer to a neighbouring type *2* layer in weak (Fig. 12) and strong (Fig. 13) fields and τ_{11} is the time taken for a jump from a type *1* layer to the nearest type *1* layer.

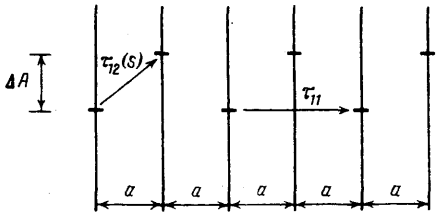


Figure 12. Schematic illustration of the energy levels of a carrier consisting of bilayers of polydiacetylene of two types differing in electron affinity ΔA by $\sim 10k_BT$ in a weak electric field ($E < \Delta A/ea$).

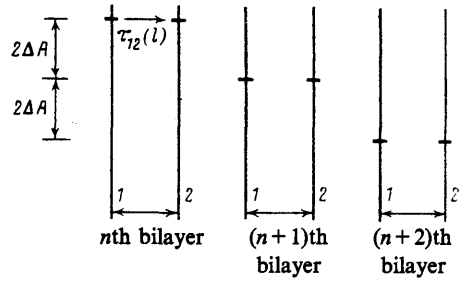


Figure 13. Schematic illustration of the energy levels of a carrier made up of polydiacetylene bilayers in a strong electric field ($E > \Delta A/ea$).

Thus $\tau_{12}(l) \ll \tau_{12}(s) \ll \tau_{11}$.

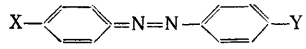
In the carrier described, one bit occupies one bilayer. For $T = 300$ K and $A = 10k_BT$, we have $\tau_{12}(l) = 8.8 \times 10^{-6}$ s, $\tau_{12}(s) = 0.19$ s, and $\tau_{11} = 2.17$ h.

The recording is carried out in a strong field $E = A/ea = 2.5 \times 10^8$ W m^{-1} for $A = 10k_BT$ at $T = 300$ K. It is stored in a weak or zero field for a time $\tau_{12}(s)$ and is read in a strong field. The storage time can be increased by using three layers for the recording of one bit (two layers of type *2* between insulated layers of type *1*). In this case, we obtain $\tau_{11} \simeq 20000$ years and $\tau_{12}(s) = 6000$ years at $\tau = 77$ K.

2. Locally reversible recording

The creation of photochemical carriers with the possibility of local re-recording of information has been reported[53]. The carrier was made from 4-$RC_6H_4CH{=}CH{-}CH{=}CHCO_2H$ (V) (R = alkyl or alkoxy-group with 6–20 carbon atoms). For example, a quartz support coated by the LB method with 162 layers of the 2-*trans*, 4-*trans*-(V) mixture (R = n-octyloxy-group) produces a carrier with an absorption peak in the region of 300 nm. Irradiation with light at a wavelength of 300 nm diminishes the intensity of this peak and at the same time a new peak appears in the region of 270 nm. On the other hand, irradiation with light at a wavelength of 270 nm restores the peak in the region of 300 nm. Thus, using two lasers, it is possible to ensure the local re-recording of information.

As stated above, in reversible information carriers based on azobenzene derivatives[37] the reverse *trans*-isomerisation reaction is hindered because of the high energy of the re-packing of molecules in the monolayer. In order to overcome this difficulty and ensure the local re-recording of information, it has recently been suggested[54] that molecules of azobenzene derivatives, i.e.

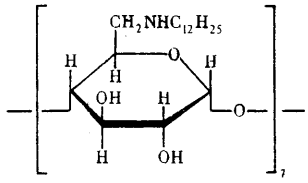


(a) X = H, Y = COOH;

(b) X = $(CH_3)_2N$, Y = COOH;

(c) X = $(CH_3)_2N$, Y = SO_3Na;

be incorporated within the cavity of the β-cyclodextrin molecule:



This seven-membered cyclic β-dextrin molecule is barrel-shaped and has an inner cavity approximately 50 nm in diameter. The *trans*-isomer of the azobenzene derivative and β-cyclodextrin (molar ratio 1 : 1) are deposited in the form of a LB film comprising 50 monolayers. The azobenzene molecule is then located within the β-cyclodextrin cavity in such a way that its long axis coincides with the axes of the aliphatic substituents in the β-cyclodextrin and the *cis–trans* isomerisation of azobenzene can be readily achieved on treatment with light in the visible or near UV regions.

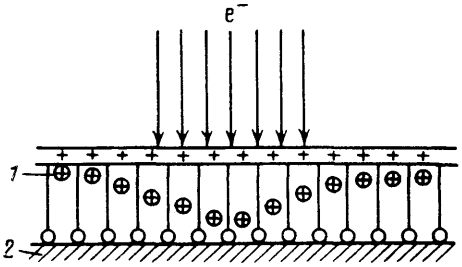


Figure 14. Carrier comprising a barium stearate LB film with mobile barium ions: *1*, barium ions; *2*, carbon base.

IV. Recording of information by an electron beam on a LB film with mobile ions

It has been proposed in a patent[55] that a LB film of barium stearate (Fig. 14) with mobile barium ions, deposited on a carbon base, be used as the information carrier. The LB film has an electrical surface potential of 100 mV relative to the base. If a

potential of +2.5 V is applied to the latter, then the excess barium ions migrate to the surface of the film.

Recording is achieved by means of an electron beam ($I = 10^{-10}$ A, $E = 1.6 \times 10^{-17}$ J, $d = 10^{-8}$ m). When it reaches the site where the information bit should be recorded (for example "1"), the potential of the support is reduced to zero by means of a synchronised potential source. A negative field gradient relative to the support is generated. However, it is insufficient for the migration of the ions to the support. Under the influence of the electron beam, the ions migrate into the bulk of the film. After the information bit has been recorded, the surface potential is reduced at this site by 0.1 V and the surface has a higher secondary emission coefficient. The information is read by secondary electron spectroscopic methods or by the diffraction of low-energy electrons using an electron beam with a current of $10^{-11}-10^{-12}$ A. The density of the recording reaches 10^{16} bits m^{-2}. Local deletion of information in this method has not so far been attained.

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