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Organic dyes for constant memory optical discs

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ABSTRACT. Literature data on the use of organic dyes in constant memory optical discs and information recording by semiconductor laser irradiation in the 780–830 nm range are summarised and systematised. Questions on the suitability of the properties of different classes or organic dyes for the main requirements of optical information-recording media have been considered. Future trends in the development of the field of organic dyes for the laser recording of discrete information have been defined.

Bibliography includes 232 references.

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I. Introduction

Optical information disc drives have a number of advantages over magnetic discs (higher recording density, possible contact-free reading, storage life of recorded information, etc.) and have been increasingly used abroad over recent years. They are mainly used in the external memories (EM) of computers. The recording of information on an optical disc is achieved by a focused laser beam, which deposits a particular trace on the surface of an active layer. The recorded information can be read by the same laser at lower power by measuring changes in the characteristics of the reflected beam.[1–5]

Memory recordings may be assigned to one of three categories with respect to the type of the recording/reading regime and the properties of the support: 1) permanent external memory devices with single recording and multiple reading (DRAW or WORM) and reversing facilities. The present review is concerned with the use of organic dyes with the DRAW type of optical discs.

The optical disc consists of a profiled support on to which an active layer <1 μm in thickness is deposited. The reaction of the laser beam on the light-sensitive layer may involve different mechanisms. The ablation process has been most extensively used. In this process the energy of the laser pulses with a duration of $\leqslant 1$ μsec is converted into heat energy causing an increase in temperature of up to 1000 °C or more at the point of exposure, leading to melting of the film, and the material is therefore unsuitable since it vapourises or decomposes. As a result of this process pits $\lesssim 1$ μm in diameter are formed. The information is read by a laser beam of energy less than the threshold value by measuring the difference in the reflectivity from the pit and the background surface. A quantitative characteristic of the recording is the signal/noise ratio at the point of recording (CNR, carrier-noise ratio).[6–9]

The recording LWR-(laser write and read) medium of the optical disc may have a mono-, bi- or tri-layer structure. A metal monolayer transferred on to the support by vacuum evaporation as a thin (ca. 30 nm) film is the most extensively used structure. The recording leads to a decrease in the reflection from the surface of the pits relative to the background. In the bi-layer (antireflex) structure the metal film is covered by a layer of organic dye $\leqslant 100$ nm in thickness. This leads to a decrease in the reflection from the surface of the recording layer of up to ca. 5% and to an increase in its sensitivity. In the pits obtained by ablation the reflectivity increases by up to ca. 90%. In the tri-layer structure the absorbing layer is separated from the metallic mirror by a transparent dielectric which leads to an increase in the efficiency with which the laser beam energy is utilised, i.e. to a further increase in the sensitivity of the material.[8,10] An increase in the number of layers of accurately controlled thickness naturally creates complications in the preparation and also leads to an increase in the price of the optical disc. The recording medium is a key component of the optical disc and should provide higher sensitivity to laser irradiation (ca. 10^{-2} J cm^{-2}), high recording resolution ($\geqslant 1000$ lin mm^{-1}), adequate recording contrast (CNR > 50 dB) a real time recording with immediate reading, and also an adequate storage period for the recording ($\geqslant 10$ years).[8–12]

Gas lasers were used in the initial stage of development of the optical discs of computer memories. Since the beginning of the eighties solid body diode lasers were most widespread and had a number of advantages such as low cost, small dimensions, long storage period, in-use stability, and the possibility of rapid change-over. Present-day optical memory systems are based on the use of GaAlAs semiconductor lasers with emission in the 780–850 nm range.[13–15]

II. Optical disc recording layers based on organic compounds

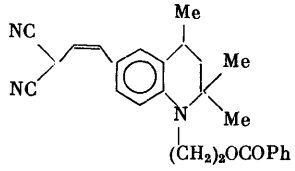
Systematic screening of metals and chalcogenides to identify optimal materials for photothermal recording showed that tellurium and its alloys possess the best characteristics,[5] although it is difficult to produce optical discs based on these materials, since tellurium readily undergoes oxidative degradation in a moist atmosphere.[14] This finding created interest in LWR-media based on organic dyes, since on account of their high stability and low toxicity they are more marketable than Te-containing layers.[11]

Carlson was first to propose the use of organic materials for laser recording in 1969.[16] Recording with a helium-neon laser beam on to a film containing a triarylmethane dye in nitrocellulose was achieved at the expense of the decolourisation of the dye. Two new

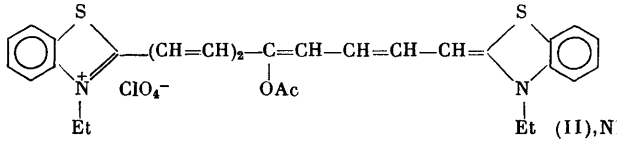
laser recording processes in an organic dye were subsequently proposed. In the first process a bi-layer structure of a polymeric dye was used. In the presence of argon-laser irradiation the dye diffused into the polymeric substrate, thereby causing a change in the spectral characteristics of the layer. 1,4-Diaminoanthraquinone and a series of polymethine dyes (PMD) on a polyethyleneterephthalate film 50 μm in thickness were used as the recording system.[17]

The second process which later became extensively used involved recording with a laser beam through ablation on a film of an organic dye deposited by vacuum evaporation on to a reflecting surface (an aluminium layer 30 nm in thickness on a glass support).[18] With a layer of fluorescein 58 nm in thickness 90% of the incident light was absorbed. The recorded information was ready by means of the difference in the reflectivities from the surface of the pits formed during the recording from the dye layer. This material was superior to the mono-layer structures based on metals in regard to sensitivity and contrasting.[18]

A defect in this system is the possibility of crystallisation of the dye in the sprayed state leading to a decrease in the CNR value.[18] Law et al. were able to surmount this process,[19] by proposing that the dye dissolved in a polymeric matrix should be used as the absorbing layer. A polyvinylacetate film 59 nm in thickness and containing 20% (by mass) of dye (I) when transferred on to a reflecting layer of aluminium provided a higher degree of sensitivity and contrast during recording with a helium-cadmium laser than layers based on tellurium. Similar bi-layer structures based on organic dyes sensitive in the visible range of the spectrum were later described in several reports.[20,21]



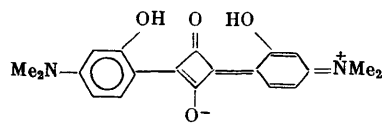
The first report on a DIP-system (dye in polymer) sensitive to irradiation in the near-infrared region of the spectrum appeared in 1981.[13] A film 105 nm in thickness containing 20% PMD (II) in polyvinylacetate transferred on to an aluminiumised glass support exhibited 3.5-fold higher sensitivity than a 15 nm tellurium monolayer during recording with a laser beam with λ_{gen} = 835 nm.



(II), NK-1748

The absorption spectra of dye (II) in the film and in methanol are presented in Fig. 1.

In the same year publications appeared on the use of vanadylphthalocyanine[22] and squarylium dye (III) [23] absorbing in the near-infrared region for laser recording.



In order to use the organic dye as a reflecting type of recording medium in a mono-layer structure, it was essential that the film formulated from the dye had adequately high reflectivity. Data confirming that this was the case were obtained for the first time in 1983.[24] It was shown that a film of a naphthaquinone dye 50 nm in thickness transferred by vacuum deposition on to a polymethylmethacrylate (PMMA) support and absorbing more than 40% of the incident light at a reflectivity of >20% provides adequate sensitivity towards irradiation of the diode laser and good recording characteristics (CNR > 50 dB at a pulse power of ≤5.5 mW).

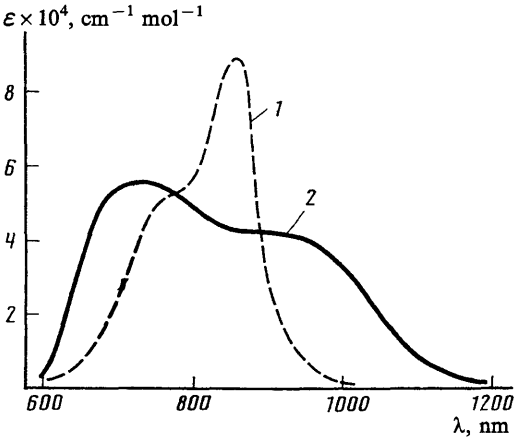
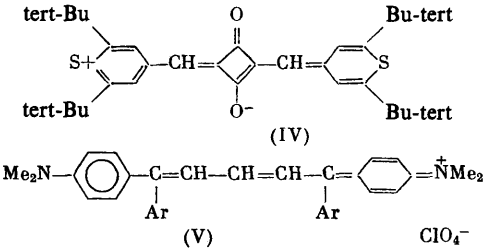


Figure 1. Absorption spectra of dye (II) in methanol (*1*) and in a poly(vinyl acetate) (*2*).

Even higher CNR values were found by certain authors with mono-layer structures obtained by spin-coating of solutions of dyes (IV) and (V) on to profiled PMMA and glass discs.



(IV)

(V) ClO_4^-

As already mentioned above the formation of pits in the LMR type of recording media is largely a photothermal process in which incident light energy is converted into heat more efficiently the more effective is the light absorption and the subsequent oscillatory relaxation of the dye molecules. By studying the mechanism of this process in the DIP-layers as described in earlier reports,[6,23,26,27] and by comparison with layers based on tellurium and other metals, it was possible to determine the optimal characteristics of the recording media and the recordings on them. The laser beam power was 5–10 mW when the diameter of the latter was 1 μm, the threshold energy of the recording was 0.1–0.2 nJ/bit, the energy essential for

the total opening of the pit and to obtain a satisfactory CNR (50–60 dB) was 0.5–1.0 nJ/bit, the optimal thickness of the layer was 60–120 nm, and the recording time was 50–100 nsec. In order to attain these values, the recording material should possess a high extinction coefficient (ca. 10^5 M^{-1} cm^{-1}) at the recording wavelength, low thermal conductivity (5×10^4 cal sec^{-1} deg^{-1}) and thermal capacity, and also a sufficiently low melting point and vaporisation temperature (100–250 °C).

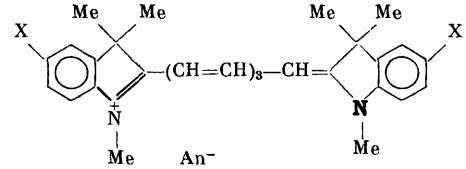
Chemical and photochemical stability under the disc storage conditions and also resistance to the action of the reading beam are important properties determining the suitability of organic dyes as active media in optical memory discs.[15] Testing of the recording layers involves maintenance at an elevated temperature (35–70 °C) in a moist atmosphere (90–95% relative humidity), illumination with visible light at ⩾50 000 lux, and continuous reading over a prolonged period.

The characteristics of the DIP-layer are dependent not only on the absorbing dye but also on the properties of the polymer. Determination of the threshold energy of the recording on DIP-layers of dye (I) with different polymers (polyvinylacetate, polyvinylbutyral, PMMA, polycarbonate, etc.) showed that the viscosity and vitrification temperature of the latter do not affect the sensitivity of the recording material.[28] Nevertheless the pit size and hence the quality of the recording is dependent on the viscosity, due to the arisal of a reverse inflow of the pit after the recording.[7] A series of review articles have already been published in which the main criteria determining the selection of components (dyes and polymers) for such materials, their ratios, and the optimal physical and chemical properties of the polymer supports have been formulated.[9,11,15] These questions have been discussed in detail in the review by Pearson.[29] The further advancement in organic recording media for optical memories based on semiconductor lasers is mainly associated with the intensive development of studies of the synthesis of thermally and photochemically stable organic dyes exhibiting intense absorption in the near-infrared spectral range and the testing of these compounds in recording systems. The present state of the art and the potential for advancements in the field of infrared dyes for optical discs are described below.

III. Dyes for optical discs with absorbance in the near-infrared region of the spectrum

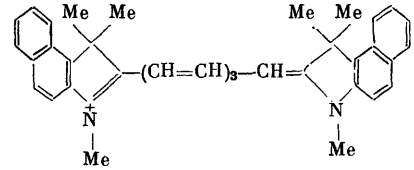
1. Polymethine dyes

Polymethine dyes have been most extensively used in laser recording, since the PMD films possess sufficiently high reflectivity (up to 40%) which provides a high degree of recording contrast.[11,14] Symmetrical polymethine dyes containing indolenine, quinoline, benzthiazole, benzoxazole residues etc. as terminal groups are most often used. Absorption in the region of semiconductor laser generation is achieved in the presence of a chain of seven or more methine groups† in the dye molecule, and therefore 1,1'3,3,3',3-hexamethylindotricarbocyaniniodide [dye NK-125 (VI),[38–41] its perchlorate,[42–44] the 4- and 5-chlorosubstituted dyes (VI) [45,46] including dye NK-2882 (VII),[47–49] 1,1,3,3,3',3-hexamethyl-4,4',5,5'-dibenzo-2,2'-indotricarbocyaninperchlorate (dye NK-2014, VIII)],[38,50–59] and 3,3'-dimethylthiatricarbocyaniniodide[60–63] are most often described in the patent literature as dyes for optical discs.



(VI), NK-125 : X = H, An = I^-

(VII), NK-2883 : X = Cl, An = ClO_4^-



(VIII), NK-2024, $\lambda_{max\ abs}$ = 782 nm

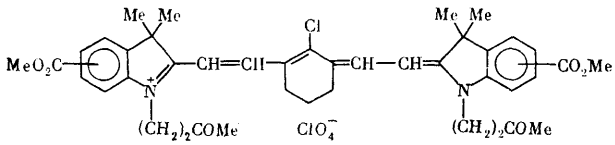
Heterocyclic nitrogen atoms in molecules of such dyes may in addition to the methyl group contain alkyl or substituted alkyl groups (Et, Pr, Bu, C_2H_4OH, etc.),[30–35,37,53,64,65] whereas the aromatic rings contain electron acceptor or electron donor substituents.[31–36] These spectra contain intense absorption bands in the 740–780 nm range. At a given polymethine chain length the benz[c,d]indole derivatives are the most deeply coloured.[66]

The polymethine colour may be deepened by increase in the length of the outer polymethine chain of the dye. In the symmetrical polycyanines an increase in length by one vinylene group leads to the displacement of the absorption maximum by 90–100 nm to longer wavelengths.[67] Thus the first dye in the polymethine series used to record information with the semiconductor laser was tetracarbocyanine(II).[13] However it is known that an increase in the number of vinyl groups to 4 or more leads to a sharp fall in the extinction and to the leveling of the absorption curve as a result of *trans-cis*-isomerisation in the polymethine chain.[68] In this case the thermal and photochemical stability of the dye also falls significantly.[69]

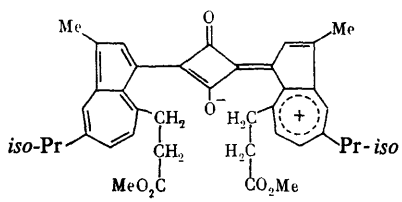
One approach by means of which a bathochromic effect may be obtained and at the same time the stability of the polymethine dye molecule is increased involves the cyclisation of part of the chromophore by bridging groups which rigidly fix the separate units of the polymethine chain.[69] There are a number of patents describing the use in optical discs of indo- and thiatri(penta)carbocyanines containing a di- or trimethylene bridge in the outer polymethine chain.[70–80] Thus a film of dye (IX) 75 nm in thickness transferred by spin-coating on to a glass support has a reflectivity of 37% and provides adequate sensitivity to semiconductor laser irradiation at 830 nm and high CNP values. The recording was stable when maintained at 50 °C in a moist atmosphere (after 150 h the CNP value decreases by 3% or more) and was stable to illumination with a 500 W daylight lamp (after 100 h the decrease in

† The use of dicarbocyanines with a maximum absorption up to 700 nm for recording with the semiconductor laser has been described.[30–37]

CNP was ⩽4% or less).[72] Hydrated aromatic or heteroaromatic rings may serve as the bridge.[11,81,82]



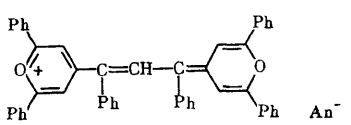
Polymethine dyes containing a squaric acid or a croconic acid fragment between the heterocyclic residues is widely used in laser recording materials.[12,14,26,83–85] Synthetic routes for squarylium dyes with absorbance in the near-infrared range of the spectrum have been described.[86] Their absorption maxima are displaced relative to the spectra of the corresponding symmetrical polymethine dyes with linear polymethine chains by 20–60 nm to longer wavelengths. The largest number of patents describe the type (X) squarylium dyes containing azulene rings[87–89] or their aza-analogues[90] as terminal groups. Active layers based on



(X), $\lambda_{max\ abs}$ = 773 nm

diazulyltri- and diazulylpentamethincyanines, which contain identically or differently substituted azulene rings, have been described.[91,92] Their absorption spectra are similar to those of polymethine dye derivatives of indolysine[93] which are also used in optical discs.[94] Replacement of hydrogen atoms in the azulene rings by alkyl groups leads to a bathochromic shift of the longwave band in the electronic spectrum and to an increase in the solubility in organic media.[89,92]

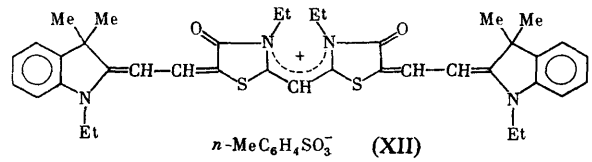
Intense absorption in the near-infrared region of the spectrum when the polymethine chain length is comparatively short may be achieved by replacement of the nitrogenous heterocycles in the polymethine dye molecules by pyrylium or thio- or selenopyrylium residues. Pyrylo- and thiopyrylocyanines containing three or five methine groups exhibit intense absorption in the 680–880 nm range and are suitable for recording information with the laser.[60,95–98] A film of dye (XI) 100 nm in thickness showed high sensitivity and good recording quality at 790 nm (stability to visible light at 54 000 lux for 50 h).[95]



(XI)

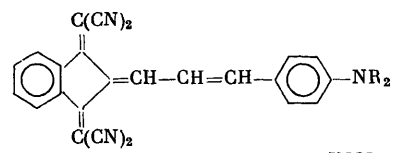
Good results have been obtained with type (IV) squarylium dyes containing pyrylium or thiopyrylium rings.[11,14,26,99] The presence of tert-butyl groups in the dye molecule increases it solubility in organic media and facilitates the formation of active layers by the spin-coating technique.[26]

There are relatively little data on the use of hemi- and mercocyanines for optical recording. Derivatives of indolenine, oxoindolysine, and pyrylium salts and their heteroanalogues,[12,100–107] assymmetrical polymethine dyes containing the azulene ring,[108–110] and also three- and four-nuclear polymethine dyes containing branched or linear chromosphores have been described.[11,112] Thus recording



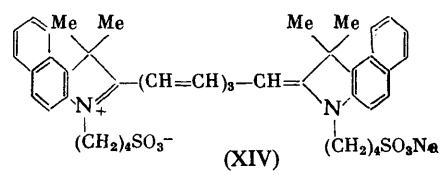
at 790 nm on a film of dye (XII) deposited on to a PMMA support by spin-coating gave a highly contrasted image stable to visible light.[111]

The identification of recording media for optical discs among the deeply coloured neutral polymethine dyes type (XIII), the dicyanomethyleneindan residue or its sulphur analogue serving as the acceptor group would appear to be a promising approach.[12,113,114]



(XIII)

Essentially the only method for the formation of thin polymethine dye films on formatted substrates of the optical discs is the spin-coating of their solutions in organic solvents,‡ dichloroethane and methyl ethyl ketone being most often used. Aqueous or aqueous-alcoholic solutions are used only for type (XIV) dyes, the latter molecules

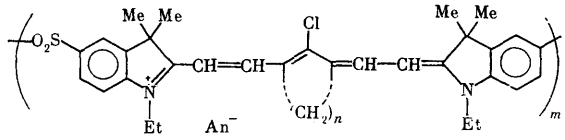


containing alkylsulphonate groups in positions 1 and 1′.[75,115]

The low solubility of polymethine dye salts in organic solvents and their tendency to crystallise are factors which hinder the production of homogeneous amorphous films which are stable and which have a suitable absorption coefficient in the semiconductor laser generation range. The most widely used method providing a means of surmounting this obstacle involves the creation of DIP-films. Nitrocellulose is most frequently used for this purpose,[55,57–59,97,102,104,106] and there are references in the literature on the use of polyvinylbutyral, PMMA and a number of other polymers and copolymers.[39,40,51,56,76,83,88] The preparation of

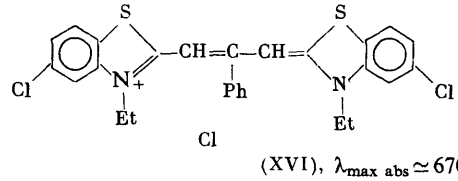
‡ Vacuum deposition may be used only for the squarylium type of polymethine dyes.[12,84]

recording layers based on type (XV) polymeric dyes has been described.[116,117] A positive effect is apparently achieved on deposition of a layer containing a mixture of two dyes.[44,118,119]

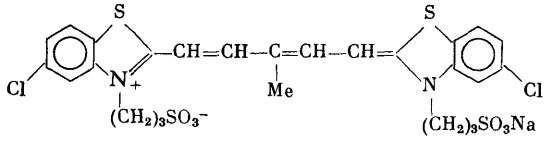


(XV) n=2, 3

Langmuir–Blodgett technology is a novel and extremely promising means of deposition of recording layers on to the reflecting supports.[120] Layers based on *J*-aggregates§ of dyes (XVI) and (XVII) exhibiting absorption in different spectral regions and obtained by this method have been described.[121]



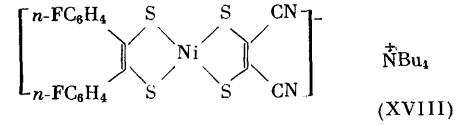
(XVI), $\lambda_{max\ abs} \simeq 670$ nm



(XVII), $\lambda_{max\ abs} \simeq 800$ nm

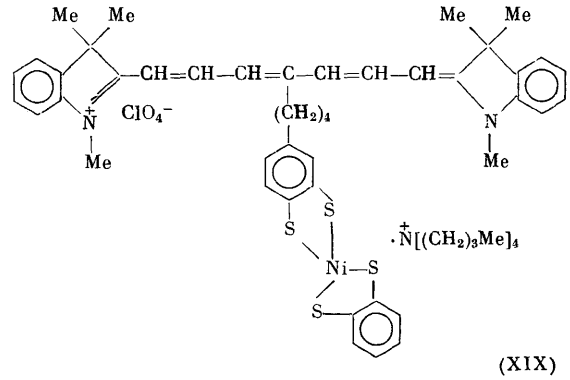
The structure of the layer containing these dyes in the Langmuir–Blodgett films and the change in its spectral characteristics by the action of a diode laser at 780 nm and xenon flash-lamps are presented in Fig. 2. The authors propose that an eight-fold spectral thickening of information is possible in the 400–800 nm range when the layer thickness of each dye is 10 monolayers, and at a total LWR-layer thickness of 250 nm and a *J*-aggregate absorption band width in the order of 50 nm.

Poor light stability is known to be a feature of polymethine dyes. There is relatively little information on the mechanism of discoloration of these dyes, although it has been proposed that an oxidative mechanism is responsible for this process.[122] In this regard recording layers based on polymethine dyes usually include singlet oxygen at a level equivalent to 10–50% of the mass of the dye. Derivatives of aliphatic and aromatic amines,[52,63,85,123] nickel acetylacetonate,[76] or titanium acetylacetonate[65] and also other transition metal complexes are used as stabilisers. Aliphatic or aromatic azomethines,[58,59,124] and derivatives of *o*-phenylenediamine, *o*-oxy- or *o*-aminothiophenol etc.,[49,55,547] may serve as organic ligands in these layers. The most widely used compounds are dithiobenzyl nickel and its substituted analogues,[61] and dithienes (dithiolates) of nickel and other transition metals.[41,42,48,53,54,98,100,125–127] Anionic salts of nickel dithienes possessing high sensitivity to atmospheric oxygen are particularly effective stabilisers.[128] There are patent data indicating that the introduction of 15% quencher (XVIII) into a recording layer based on polymethine dyes reduced the extent of its degradation by 75–80% on exposure to visible light.[125,126]



(XVIII)

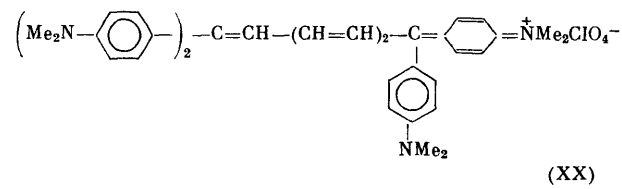
The light stability of the active layer and the repeated information reading may be significantly increased, when nickel salts of polycyanines containing alkylsulphonate or alkylcarboxylate groups at the heterocyclic nitrogen atoms are used in the LWR-layers,[129–131] and also when polymethine dyes containing nickel dithiolate fragments in the molecules are used.[132] Thus degradation of dye (XIX) in the presence of light is five-fold lower and stability to reading is ten-fold higher than those in the case of dye (VI).[132]



(XIX)

2. Dyes in the di(tri)arylmethane and triarylamine series

Triphenylmethane dyes with intense absorption in the visible range were some of the first dyes to be tested in recording layers of optical discs.[16,18] Examples of their use in computer external memories based on semiconductor lasers later appeared.[12,139] Absorption in the infrared range is achieved by introduction of chains of two or more vinylene groups into their molecules,[133–139] and in a number of cases by incorporation into the rings.[12,139] A similar effect is obtained, when the benzene rings are replaced by heteroaromatic residues,[140] and also when a squaric acid residue is introduced into the chain.[141] Type (XX) arylmethane dyes containing dialkylamino groups in *para*-positions of the aromatic rings have been most extensively used.[133–138,141]

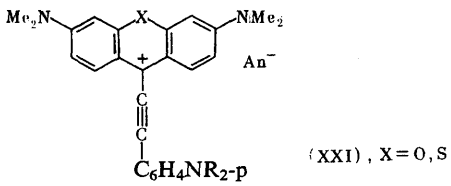


(XX)

It has been shown that the binding of two phenyl rings in the triphenylmethane dye molecule by means of a heteroatom containing unshared electron pairs leads to a deepening of the colour.[122,142]

§ *J*-Aggregation, aggregation of the dye molecules leading to the displacement of absorption to longer wavelengths.

The opposite effect was obtained by Japanese chemists on introduction of an acetylene group between the central carbon atom and the *p*-dialkylaminophenyl residue in the type (XXI) dye molecule.[143] Films of such dyes in polymer supports show adequate stability and are appropriate for laser recording.[144,145]



(XXI), X = O, S

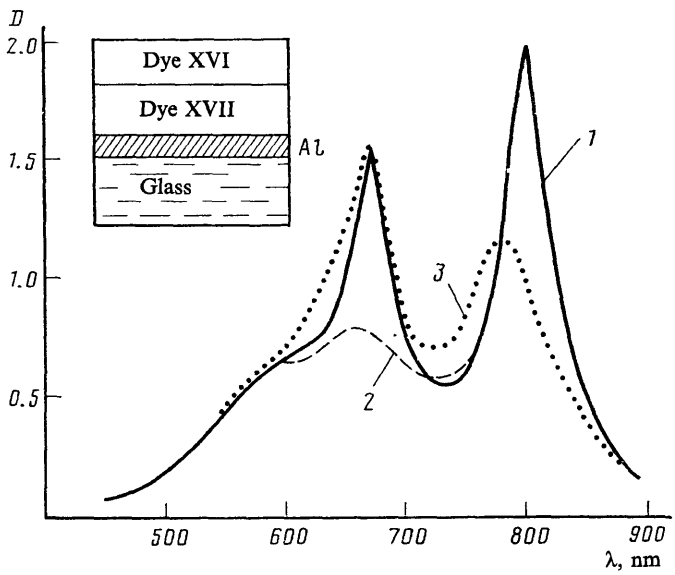
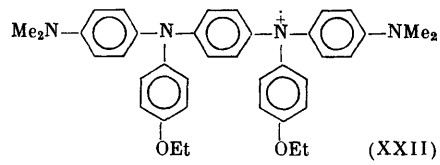


Figure 2. Absorption spectra of a Langmuir–Blodgett film containing layers of dyes (XVI) and (XVII) before irradiation (*1*), after irradiation with a xenon flash-lamp (*2*) and after irradiation with a diode laser at 780 nm (*3*).

Cationic arylmethane dyes have been tested in both mono-layer and bi-layer structures of LWR-materials. They may be deposited on to profiled supports by spin-coating of solutions in dichloroethane, methyl ethyl ketone, dimethylformamide, or some other organic solvent. Polymer additives (PMMA, nitrocellulose) or crown-ethers are used to form the film.[133,134] By using these additives a wider range of solvents will be suitable for this purpose.[138] Although the triarylmethane dyes share the common property of reduced light fastness,[122] there are patent data which describe the creation of films based on type (XX) dyes which have adequate resistance to the action of visible light[135] and to prolonged heating in a moist atmosphere.[139] The light fastness may be improved by introduction of nickel dithiolates into the recording layer.[137]

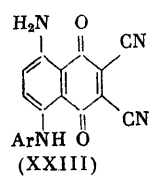
Triarylaminylic salts (the electronic spectra of which contain broad absorption bands in the near-infrared range) have also been proposed as dyes for optical discs.[142,146,147] Despite the cation-radical nature of these compounds and their thermal instability in solution there are patents describing the preparation of dye (XXII) in a film for the laser recording of a contrasted image stable to prolonged irradiation from a daylight lamp.[147] However, this type of dye is most often used in a mixture with a polymethine dye as a singlet oxygen quencher.[37,54,80]



(XXII)

3. Quinone and quinonimine derivatives

Calculation of the electronic absorption spectra of aminosubstituted naphtho- and anthraquinones shows that the longwave absorption band results from the $\pi-\pi^*$-transition involving the transfer of electron density from the benzene to the quinoid ring.[142,148] Consequently this band may be displaced to the near-infrared region as a result of the introduction of donor groups into positions 5 and 8 or acceptor substituents into positions 2 and 3 of the 1,4-naphthoquinone molecule. In accordance with this observation in 1983 it was shown that 2,3-dicyano-5-arylamino-8-amino-1,4-naphthoquinone (XXII) derivatives absorb in the 760–800 nm range and may be used in optical discs as the reflecting type of recording medium in the monolayer structure.[24,149,150] The synthesis of type (XXIII) dyes has been described in detail.[151]

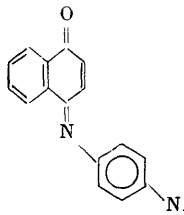


(XXIII)

In later years many patents have appeared on the use in laser recording of type (XXIII) dyes with different substituents (Alk, Hal, OR, NHR, NHAr, etc.) in the aryl residue.[12,14,152–162] The structure of the dye has a specific effect on the absorption range, and on the sensitivity and stability of the active layer. The best results were obtained with *p*-alkoxy-substituted compounds.[14,157,158,160] Other authors have shown that introduction of the methoxy group into the *para*-position of the N-aryl residue increases the stability of the recording from several months to ca. 10 years.[158]

The neutrality of the naphthoquinone dyes confers good solubility in organic media and high stability. Films of such dyes may therefore be formed on the supports by spin-coating and vacuum deposition.[151–162] At a thickness of 60–200 nm they have adequately high reflectivity ($\gtrsim$30%) and it is therefore possible to use them in monolayer structures without a metallic reflecting layer. Recording by GaAlAs-laser irradiation at 830 nm and an impulse strength of 4–10 mW provides a CNR value of more than 50 dB.[152,153,162]

In recent years the search for new naphthoquinone dyes for optical discs has advanced in several directions. One of these directions involves the use of the 1,4-naphthoquinone-4-imine (XXIV) structure containing the *para*-dialkylaminophenyl group in the nitrogen atom.[163]



(XXIV), $\lambda_{max\ abs} \simeq 580$ nm

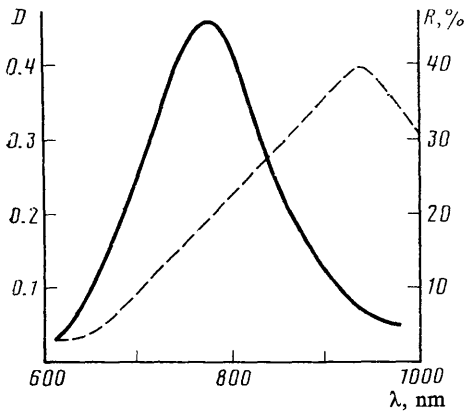
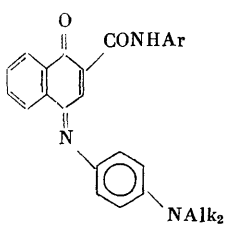


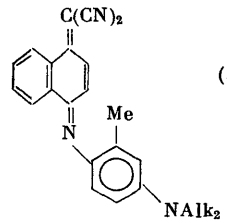
Figure 3. Absorption spectra and the reflection of a layer of dye (XXVI) in PMMA 60 nm in thickness.

Introduction of acceptor substituents into the quinoid moiety of the type (XXIV) dye molecule leads to the appearance of an intense absorption band with a charge-transfer in the near-infrared range which confers sensitivity to semiconductor laser irradiation.[163] Data in Japanese patents confirm that indoaniline dyes (XXV) may be used in mono- and bi-layer structures for laser recording at 780 nm.[164,165]



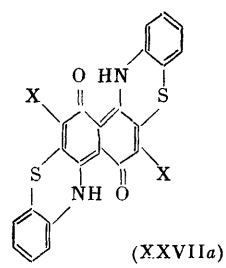
(XXV), $\lambda_{max\ abs} \geqslant 720$ nm

Displacement of the longwave absorption band into the infra-red range may be attained also as a result of the replacement of the oxygen atom in structure (XXIV) by the dicyanomethylene group. Synthesis of type (XXVI) dyes has been described.[166,167] Their films transferred on to a polymeric support have a broad absorption band in the 600–1000 nm range in the electronic spectrum and adequate reflectivity (Fig. 3) which provides excellent recording characteristics at 830 nm at a laser pulse power of 4 mW.[166–168]

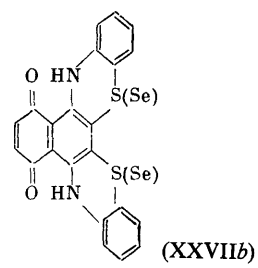


(XXVI), $\lambda_{max\ abs} \approx 760$ nm

Another approach for obtaining the quinoid type of infrared-absorbing dyes is the creation of structures (XXVII*a*, *b*) based on the 1,4- and 1,5-naphthoquinone molecules and containing azine heterocycles.



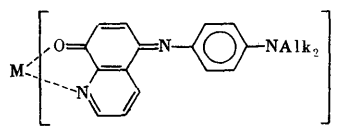
(XXVII*a*)



(XXVII*b*)

Compounds of this type have been obtained by interaction of a 6-X-substituted 2,3-dichloronaphthazarine with a salt of *o*-aminothio(seleno)phenol. Spectral studies showed that they exist in the quinoid form and that the introduction of *peri*-located phenylamino groups into the azine rings leads to a bathochromic shift of the longwave absorption band by 50–100 nm.[148,150,169,170] The 1,5-bis(phenothiazin)quinone (XXVII*a*) absorbs in a region of longer wavelengths in comparsion with 1,4-naphthoquinone (XXVII*b*).[170] An additional bathochromic shift is found for the disulphoxide, compound (XXVII*b*), owing to an increase in the electronegativity of the azine ring.[170] Bis(phenothiazine)quinone films 20–110 nm in thickness transferred to polymeric supports by vacuum deposition have been tested as a recording medium for use at 780 nm in mono-layer structures and were found to exhibit adequate thermostability.[169,171,172]

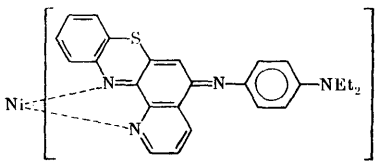
The stability of recording layers based on naphthoquinone dyes may be significantly increased by complex formation with cobalt salts.[158] This observation marked the beginning of a series of studies on the molecular "design" of infrared-absorbing dyes by creating transition metal complexes based on 1,4-naphthoquinone or 1,4-naphthoquinone-4-imine derivatives.[173–176] Complex formation leads to the appearance of an intense band with a charge-transfer in the near-infrared range. Its longwave shift relative to the absorption band attributable to the $\pi-\pi^*$-transition in the ligand molecule is 140–170 nm for type (XXVIII) structures.[175]



M=Ni, Co, Cu

(XXVIII), $\lambda_{max\ abs}$ ca. 770 nm

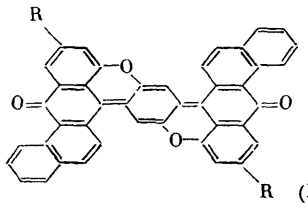
An even greater bathochromic effect is obtained during complex formation of pyrido-[2,3-a]phenothiazine dyes. For example when complex (XXIX) is obtained from the corresponding ligand, the longwave absorption band is displaced by 184 nm, and there is a 4,9-fold increase in the molar coefficient of extinction.[177,178] The complex of physical and chemical properties of type (XXVIII) and (XXIX) dyes determine their potential in the field of optical disc recording.



(XXIX), $\lambda_{max\ abs} = 838$ nm

There are relatively little data on the use of anthraquinone dyes in memories based on diode lasers. The patent and scientific literature describe anthraquinone derivatives containing the amino- and arylamino groups in *peri*-positions,[179,180] including the groups incorporated into azine rings.[150,169,181,182] The spectral properties of lasers based on these derivatives and also the characteristics of laser recording in such layers are similar to the readings obtained for analogous naphthoquinone derivatives.

In recent years patent data have appeared on the LWR-layers based on vat dyes, anthrapyridone derivatives,[183] and the (XXX) type of polycarbocycles.[184] Films from these compounds



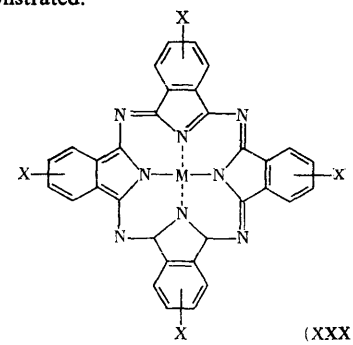
(XXX), $\lambda_{max\ abs} = 770$ nm

may be formed by vacuum deposition and by spin-coating, and they are highly resistant to heating in a moist atmosphere.

4. Phthalocyanines and other metallic complex dyes

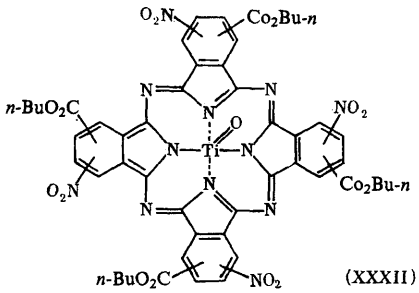
The phthalocyanines or tetrabenzotetraazaporphines are structurally similar to natural pigments based on the porphine-16-centric aromatic system. The spectra of metallised phthalocyanines contain narrow and very intense absorption bands in the 650–750 nm range. This class of dyes typically possesses extremely high thermal- and light-stability,[122,142] resulting in the use of phthalocyanines in optical disc information recording in the early stages in the development of this field.[14]

The use of phthalocyanines (XXXI) of both transition (manganese,[185,186] nickel,[187,188] iron,[188] titanium,[189,190]) and nontransition metals (magnesium,[191] zinc,[188] lead,[187,188,192] aluminium,[193,194] tin,[188,195] and silicon elements[196]) in optical discs has already been patented. The titanium, aluminium, tin, and silicon derivatives contain in the complex forming element an oxygen or halogen atom, Alk, Alko, Alk_3SiO-groups, etc. Materials based on copper[187,188,197–199] and vanadium[187,188,198,200–206] phthalocyanines have been most widely used. The possibility of laser recording on films of metal complexes of phthalocyanine thioanalogues has been demonstrated.[207,208]



(XXXI)

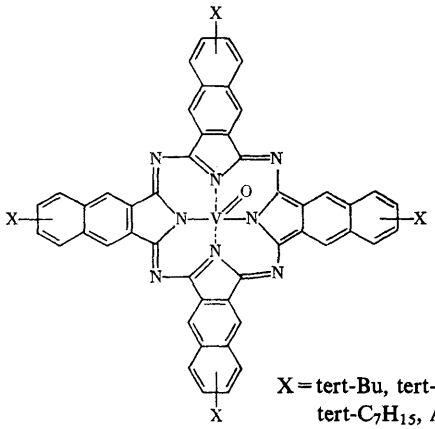
SSP molecular orbital calculations of phthalocyanine dye molecules show that excitation leads to the displacement of electron density from the centre of the molecule to its perimeter and consequently a decrease in the electronegativity of the complex forming group and the introduction of electron acceptor substituents into the benzene rings should lead to a bathochromic displacement of the longwave absorption band.[122] Accordingly in the electronic spectra of films based on titanylphthalocyanines (XXXII) containing strong electron acceptors in the aromatic nuclei



(XXXII), $\lambda_{max\ abs} = 805$ nm

absorption in the infrared range is found which provides high sensitivity to semiconductor laser irradiation and a recording with good contrast (CNR $\geqslant$ 51 dB).[189,190]

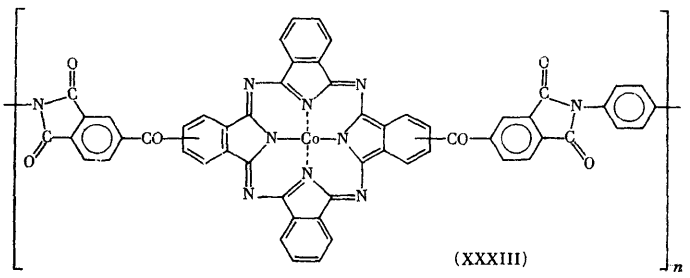
Naphthalocyanine dyes have been widely used in optical disc recording.[209–217] The extension of the conjugated system owing to linear annelation of benzene rings to form 2,3-naphthocyanine causes a bathochromic displacement of the absorbance by 80–100 nm, moving it nearer to the diode laser generation range (ca. 800 nm).[142] The same elements as those in the type (XXXI) phthalocyanines may serve as complex forming groups. Lasers based on vanadyl-naphthocyanine are most widely used.[218,220]



X = tert-Bu, tert-Am tert-C_7H_{15}, AlkS, N = NR and others

On account of their high thermal stability the phthalocyanine dyes may be deposited on supports by vacuum deposition.[185,191,195,208] Nevertheless despite the low solubility of the phthalocyanines in organic media, the spin-coating technology is becoming increasingly used.[186,189,190,194,202,209,214,216] Solubility can be increased by introduction into the dye molecule of alkyl or alkoxy groups containing three or more carbon atoms or silicon-containing residues containing long-chain alkyl groups or several halogen atoms.[186,187,194,202,204,211,214,216–219] Good recording characteristics were obtained on layers containing mixtures of phthalocyanines with polymethine dyes[43,199] and 2,3-dicyano-5-amino-8-arylamino-1,4-naphthoquinones.[221,222]

DIP-layers based on phthalocyanine dyes have been used much less frequently than those based on polymethine dyes. Nitrocellulose and polystyrene, etc. have been used as polymeric supports.[186,211,218] Excellent laser recording readings have been obtained on layers of polymeric dye (XXXIII).[223]

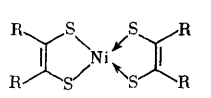


(XXXIII)

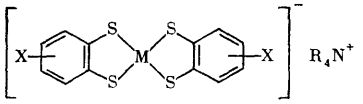
Films of metallic complexes of phthalocyanines possess relatively high reflectance in the near-infrared range and therefore may be used within both bi-layer recording materials incorporating a metallic reflecting layer (Sn,[203] Re,[224] Al[205,215,218]) and monolayer structures.[189,190,202,206] Thus a naphthalocyanine layer containing the complex-forming group $Ge(OSiEt_3)_2$ 90 nm in thickness has a reflectivity of 50% at 825 nm and provides a CNR value equal to 50 dB at a recording beam pulse power of 5.3 mW.[213]

A characteristic feature of the phthalocyanines is their high thermal and light stability.[122] The recording layers based on these compounds do not require the use of stabilisers, although a positive effect has been observed when they are supplemented with triarylaminyl salts[199,214] and titanium acetylacetonate.[200] The high operating features of the LWR-layers based on the phthalocyanine dyes and also on the inexhaustible flow of patent literature indicate that, together with the polymethine and naphthoquinone dyes, they are undoubtedly of interest in regard to the technology of the optical memory discs.

In addition to the phthalocyanines and metal-containing quinone derivatives (see previous section), metal (Ni, Cu, Co, Fe, etc.) complexes with *o*-oxynitrosonaphthalenes, aromatic azomethines, and other organic ligands have been reported as being active media for optical recording.[225,226] The extensive use of dithiolate complexes of metals and recording layers based on polymethine dyes and other dyes as singlet oxygen quenchers has already been described. Their use as supports in photothermal recording has also been described.[227–230] A large amount of data concerns both the neutral (XXXIV) [227–229] and also the anionic (XXXV) type[230,231] of nickel complexes.



(XXXIV)



(XXXV)

The metal dithiolates have low solubility in organic media which is a serious defect of these dyes, since only the spin-coating technique may be used to transfer them on to supports. Solubility may be increased by introducing into the ligand molecule alkyl groups with seven or more carbon atoms, several Me-groups, or halogen atoms[227,228,230,231] and also by creating dye-polymer compositions.[281,231] Since the metal dithiolate films have low reflectivity they may be used only in bi-layer structures with a metal reflecting layer (Al, Au).[227,228,232]

IV. Conclusion

Thus in the past decade a new direction has appeared in the field of non-silver photography, discrete laser recording on organic dyes for use in optical systems with a large capacity memory. A study of organic recording media has revealed a number of advantages over lasers based on tellurium and its alloys, i.e. high resistance to the action of atmospheric oxygen and moisture, lower toxicity, relatively low melting points conferring higher sensitivity, low thermal conductivity with the consequent attainment of a higher recording density, a comparatively inexpensive technology for disc preparation, and the possibility of altering the optical and thermomechanical properties of the recording medium by modification of the structure of the organic dye.

From the experience gained to date from the experimental study of the electronic structure of dyes and with the aid of quantum chemical calculations it is possible to conduct a targetted synthesis of dyes suitable for use in optical discs during recording with semiconductor lasers at a wavelength of 780–830 nm. The polymethine dyes, metallic complexes of phthalocyanines and naphthoquinone dyes are most promising. The growing market abroad in DRAW optical discs and the introduction of the flexible type of carrier for optical recording on organic dyes ("digital paper") are undoubtedly powerful stimulants for the further development of studies in the field of organic dyes and photothermal materials based on these compounds.

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