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MAGNETO-OPTIC POLYMERS, (U)
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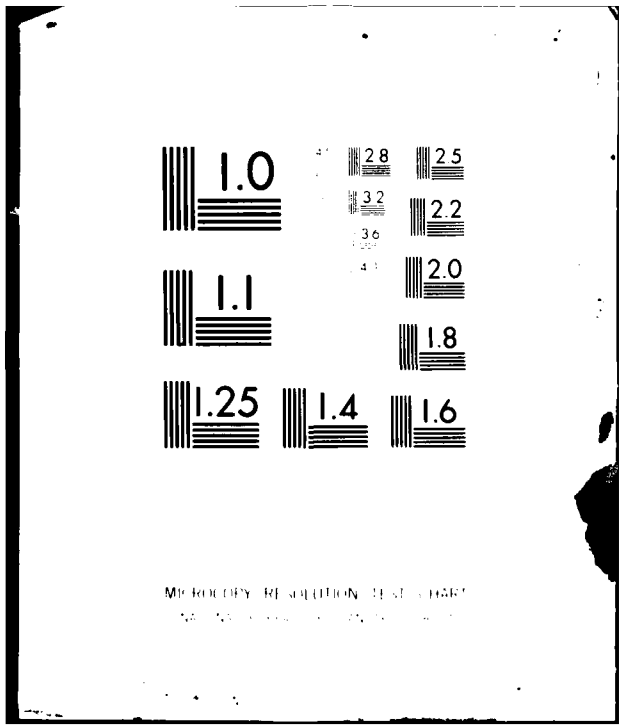
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MAGNETO-OPTIC POLYMERS

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20. Abstract <p>This was a short study aimed at looking into the feasibility of a new approach to realising a truly transparent magneto-optical material; namely fine magnetic particles dispersed in a polymer matrix.</p> <p>Particulate magnetic materials in a range of sizes, shapes and chemical forms were dispersed in a variety of polymer matrices, principally styrene.</p> <p>The samples were examined for the effect of magnetic field on their transmission of light.</p> <p>Although the samples were satisfactorily made, no significant magneto-optic effects were observed.</p>			

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PREFACE

The samples were prepared at the Central Research Laboratories of THORN EMI Ltd. Their magneto-optic responses were examined using an ellipsometer similar to that described by Champion et al (1978)*. The measurements were undertaken by Dr. G.H. Meeten of the Liquids/Polymers/Colloids Research Group at the City of London Polytechnic who would also help identify the nature of any effects detected in the samples.

* J.V. Champion, D. Downer, G.H. Meeten, S.A. Vaudrey, L.F. Gate, J. Chem. Soc. Faraday Trans II 74, 843 (1978).

MAGNETO-OPTIC POLYMERS

1. INTRODUCTION

This short study was aimed at checking the feasibility of a new approach to making transparent magneto-optic material. This was to be achieved by dispersing magnetic particles in polymer matrices. Many magneto-optic effects were thought possible and an object of the study was to determine by experiment which of these were most significant; theoretical study being deferred to a later stage.

The specific intention of this study was to produce (oriented) arrays of strongly magnetic particles in transparent polymers and to examine their influence on polarised light in the presence of a magnetic field.

A wide range of magnetic particles were examined, variations in size, shape, and chemical nature were considered. Three types of polymer were examined. To maintain high optical transmission, low particle loadings (0.005% by weight) were necessary for the 5 mm samples prepared.

Magneto-optic measurements were undertaken by Dr. G.H. Meeten at City of London Polytechnic using an adapted polarimeter with facility for applying a magnetic field along or across the direction of the light ray; optical rotation, birefringence and dichroism were looked for.

2. BACKGROUND

The origin for this project lay in reports of large magneto-optic activity observed from cobalt particles dispersed in a plastic matrix.

The nature of the effect was not determined although magneto-strictive effects of the particles on the matrix were believed to be the source of the observed birefringence.

With this thought in mind, the polymer matrix chosen for the study was polystyrene, which has a high stress-birefringence index; polymethyl methacrylate which has a low stress-birefringence index was chosen as a control.

Initial work was to be with iron oxides which are much used in the magnetic recording industry; the dispersing properties of these materials are relatively well known by these laboratories; other particles were to be used as the work progresses.

3. EXPERIMENTAL PROCEDURE

3.1 Sample Preparation (Polymer Blocks)

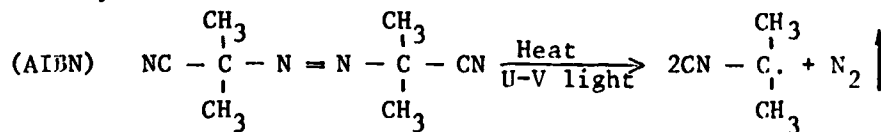
3.1.1 General Procedure

Although slightly modified (to reduce water contamination) as the project proceeded, most samples were prepared in the following way:

- 1) B.D.H. Ltd. "Laboratory Grade" styrene (or methyl methacrylate) was worked with dilute (2N) sodium hydroxide solution to remove the inhibitor (tert-butyl catechol for styrene: quinol for methyl methacrylate).
- 2) The alkali was removed by four washings with demineralised water.
- 3) The organic liquid was dried by mixing with anhydrous sodium sulphate for one hour, followed by overnight exposure to activated molecular sieve and then transferred to a stoppered bottle.

- 4) Initiator (Azo-isobutyronitrile*) was added at 0.5 - 1% by weight on monomer.
- 5) The sample was partially polymerised at 55 - 60°C in a water bath, until a viscous liquid about the consistency of motor oil was obtained. Adequate temperature control could only be achieved in a water bath.
- 6) The magnetic particles were added - usually around 0.01% by weight on monomer.
- 7) The vessel was filled to approximately 45% of its volume with 3 - 4 mm diameter lead glass balls and milled for 16 hours (overnight) on a roller mill.
- 8) The dispersed sample was decanted off the glass balls and put into moulds.
- 9) The samples were fully polymerised at 55 - 65°C in a water bath, with magnetic fields applied as appropriate.
Predispersed particles (Ferrofluids) were added at stage 4) and the ball milling process omitted.
- 10) After the samples had become rigid, the moulds were broken and suitably shaped pieces cut out for optical measurement after polishing the faces.

*Azo-isobutyronitrile



3.1.2 Modifications to Sample Preparation to Avoid Crazeing

The early sample showed a tendency to degenerate into non transparent forms. Samples prepared without any magnetic particles also underwent this change in one case, thus indicating that the particles themselves were not the root of the problem. It was decided to tighten up the drying procedure and try and use a nitrogen atmosphere whenever possible. The most recent samples show little tendency to degenerate so far.

In the final samples, the dried monomer (after stage 3) was distilled under 5 mm mercury pressure of nitrogen at 25°C through a Vigreux column and only the middle fraction was collected, as described by Lowell and Price^[1].

[The sample prepared in this way was colourless, in contrast to the samples prepared without distilling. The straw colour appears when the styrene is washed with dilute alkali to remove the inhibitor].

The polymerisation procedure then continued as outlined above, with special emphasis on using dried, cleaned equipment.

These samples were thermally polymerised in an oven rather than a water bath, to minimise water contamination.

3.2 Magneto-Optic Measurements

The magneto-optic measurements were undertaken by Dr. G.H. Meeten at the City of London Polytechnic.

3.2.1 Experimental Details

Figure 1 shows a diagram of the apparatus. Intensity changes of down to $\pm 0.1\%$ could be detected. Due however to the effect of the

* [1] A.I. Lowell and J.R. Price, J. Polymer Science 43, 1 (1960)

magnetic field on the photomultiplier tube and the flexible nature of some of the specimens, small intensity changes were sometimes found, between about 0 to 1%. Thus any changes due to the magneto-optical effects are measurable down to about 1% with certainty.

Two basic measurements were made on each specimen. (1) with the field (H) along the light path and (2) with H transverse to the light path. The magnet had axial holes for the type (1) measurements. Fields up to 3,000 oe were used, with field reversals. Where possible H was applied parallel and at 90° to the direction of the magnetic field used during the polymerisation process.

Three magneto-optical phenomena were in principle measurable. These were:

- a) a change in optical attenuation caused by H
- b) a birefringence (or linear dichroism) caused by H
- c) an optical rotation caused by H (Faraday rotation)

a) can be present with H either parallel or at 90° to the light beam direction. b) requires H to be at 90° to the light beam direction. c) requires H to be parallel to the light beam.

Most measurements were made at a wavelength of $0.5 \mu\text{m}$, where the apparatus was most sensitive. Some measurements were made using white light for specimens that absorbed heavily in the blue-green region and only transmitted red light (e.g. MO2228 films). The mean wavelength effective for these specimens was estimated to be about $0.6 \mu\text{m}$.

4. THE RESULTS

4.1 Small Particles

Polymers were loaded with very small (200 \AA) spherical particles of superparamagnetic magnetite (ferrofluids); and with slightly larger needles of iron, as used in the recently introduced "iron" magnetic tapes.

Some five samples of ferrofluid loaded styrene were prepared. Concentration ranged from 0.005 to 0.008% by weight. The ferrofluid used was D.O1 supplied by Ferrofluids Corporation of the U.S.A. All samples were well dispersed, those containing 0.005% by weight were of reasonable optical density, and later samples were successfully oriented in a 1000 oe magnetic field. These samples show optical anisotropy quite clearly.

Two samples of styrene loaded with fine iron powder were prepared. The iron particles were Magnet 1100 supplied by Hercules of the U.S.A. The particles are typically needle shaped, 0.2 to 0.3μ long and some 300 \AA in diameter.

Both polymer samples were oriented in a 1000 oe field. The powders were well dispersed and showed good optical evidence of alignment.

Neither the ferrofluid, nor the iron powder samples showed any form of magneto-optic effect greater than the measurement limit of 1% (see Table 1).

4.2 Intermediately Sized Particles

These particles were roughly the same dimensions as a wavelength of light. They were mostly needle shaped particles intended for use in

magnetic tapes, and were about 0.5μ long and 0.1μ diameter. PFIZER MO2228Hc was mostly used for this work as this is a very nicely formed needle shaped $\gamma\text{Fe}_2\text{O}_3$ pigment. As an alternative TODA PX-HC $\gamma\text{Fe}_2\text{O}_3$ powder was also tried.

Those powders were dispersed in styrene, and a few early samples were also dispersed in methyl methacrylate. Early samples were not magnetically aligned, but later ones were well dispersed and well aligned showing optical anisotropy.

A series of magnetic tape like samples were prepared from the MO2228Hc oxide, from CrO_2 particles of similar shape supplied by Montedison of Italy, and from Cobalt ferrite powder supplied by Pierce Wariner.

These dispersions contained some 30 to 35% by weight of pigment, but were coated in films a few microns thick so that they were transparent. Coatings were aligned with magnetic fields so that some samples had random orientation, others had the needles lined up perpendicular to the plane of the film, and the third set had the needles aligned along a direction in the plane of the film.

The Cobalt ferrite was not well dispersed, but the $\gamma\text{Fe}_2\text{O}_3$ and the CrO_2 samples were well dispersed and well oriented.

Neither the block polymer samples nor the more concentrated film samples showed any magneto-optic effects greater than the measurement limit of 1% (see Table 1).

4.3 Large Particles

Two types of pigment containing particles larger than a wavelength of light were investigated. One was a platelet form of magnetite -

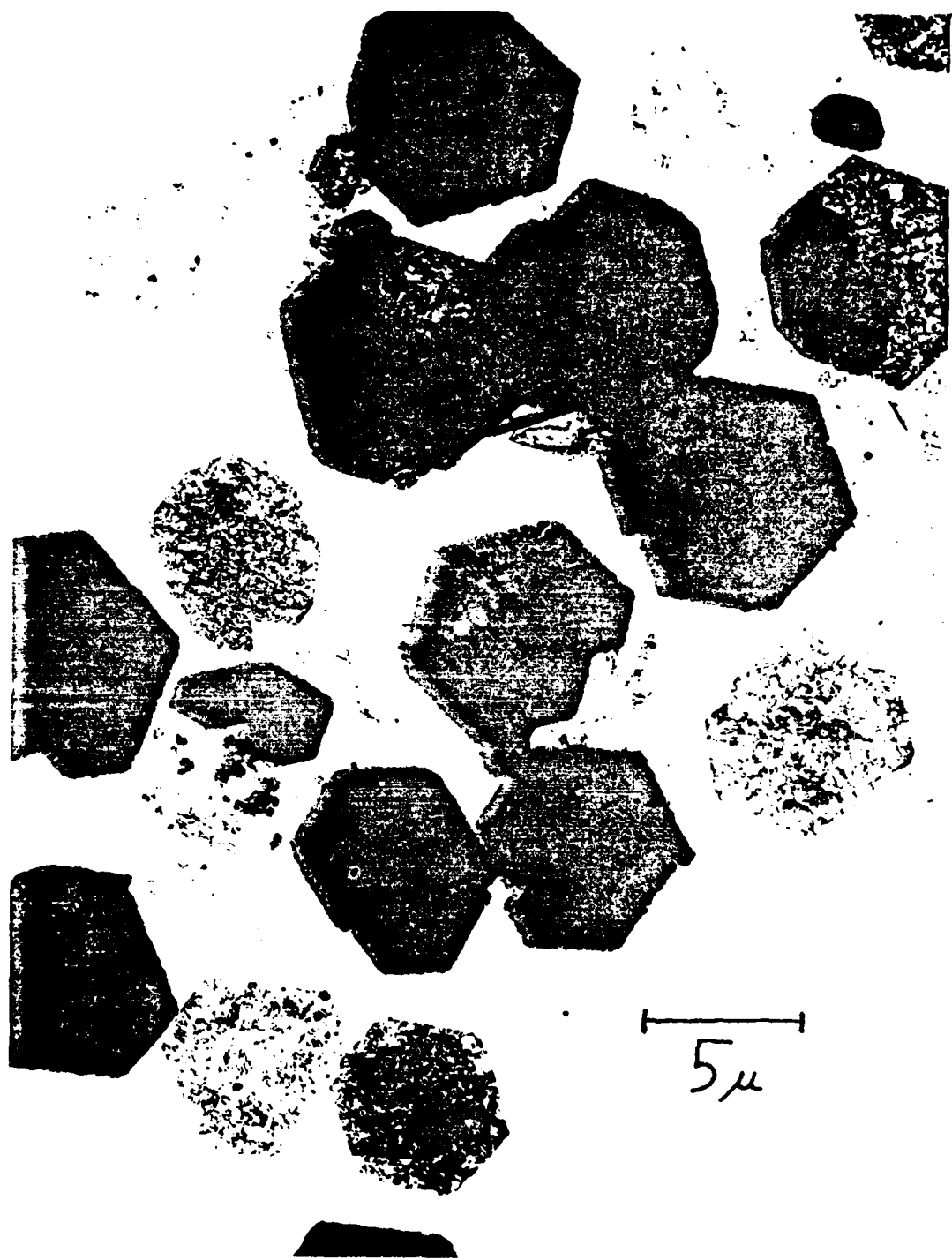


FIGURE 2 MICROGRAPH OF BAYER BX 12035M

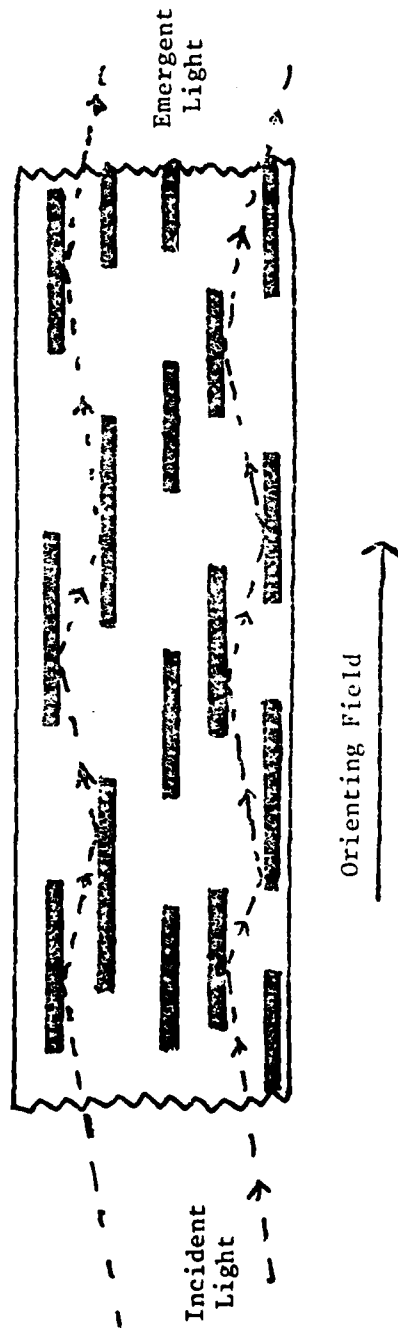


FIGURE 3 SCHEMATIC OF LIGHT INTERACTION WITH A SET OF ALIGNED PARTICLES

BXG 12035/M supplied by Bayer of Germany. This material consists of 5 micron hexagonal plates, a fraction of a micron thick (see Figure 2). These plates can be aligned in a magnetic field so that when light is directed through the sample it might be expected to undergo a series of reflections. See Figure 3.

The other pigments were of coarse iron powder, one P100 was spherical and passed through a 100 mesh, the other HOGENAS ASC100-29 contained a wide range of particle sizes. Both were intended for powder metallurgy use.

The platelet magnetite pigment was easily dispersed in styrene, but we experienced difficulty in aligning the particles as at first they migrated through the styrene due to gradients in the aligning field. This was cured by using a much more uniform field for alignment, and later samples were well dispersed, and showed marked optical anisotropy.

Styrene samples containing the coarse iron powders were made up in the usual way, but the particles were not well dispersed, and formed chains when an attempt was made to align them in a magnetic field.

In neither case were any detectable magneto-optic effects measured (see Table 1).

Sample Number	Magnetic Material	Polymer Matrix	Particle Concentration (%)	Orienting Field Applied	Field Strength(Oe)	Format	Comments	Magneto-Optic Activity
	Small Particles							
1	Ferrofluid DOI (Superparamagnetic Fe ₃ O ₄)	Styrene	0.008	No	-	Polymer Block Samples	Dark Sample	No Magneto-Optic Activity Above 1%
2	Ferrofluid DOI	Styrene	0.008	Yes	40		Same as (1) except Field Applied	
3	Ferrofluid DOI	Styrene	0.005	Yes	40		Light Sample	
4	Ferrofluid DOI	Vacuum Distilled Styrene	0.005	Yes	1000		Light Sample	
5	Ferrofluid DOI	Vacuum Distilled Styrene	0.005	No	-		Larger Sample	
6	Hercules Magmet 1100, Acicular Iron Powder	Styrene	0.04	Yes	1000		Black Sample, Well Aligned	
7	Magmet 1100	Vacuum Distilled Styrene	0.088	Yes	1000		Dark Sample Well Aligned	

TABLE 1 RESULTS

Sample Number	Magnetic Material	Polymer Matrix	Particle Concentration (%)	Orienting Field Applied	Field Strength(Oe)	Format	Comments	Magneto-Optic Activity	
	Intermediate Particles								
-8	PFIZER M.O. 2228 Hc	Styrene	0.005	No	-	Polymer Block Samples	First Samples, Very bad Crazing after three months	No Magneto-Optic Activity Above 1%	
-17	Acicular Fe_2O_3	or Methyl Methacrylate	Optimum						
18	TODA (Japan) PX-HD Acicular Fe_2O_3	Styrene	0.015	No	-				Light Brown, Hazy, with many Bubbles
19	TODA PX-HD	Styrene	0.005	Yes	40				Bubbles but some regions satisfactory no optical anisotropy
20	M.O. 2228 Hc	Styrene	0.014	Yes	700				Optical anisotropy but particles migrate
21	M.O. 2228 Hc	Styrene	0.14	Yes	1300				Uniform Field Optical Anisotropy

TABLE 1 RESULTS (Continued)

Sample Number	Magnetic Material	Polymer Matrix	Particle Concentration (%)	Orienting Field Applied	Field Strength(Oe)	Format	Comments	Magneto-Optic Activity			
22	M.O. 2228 Hc	Solvent Cast Acrylic Co-Polymer Paraloid-B72	35	No	-	Streaky Thin Film Tape Samples (2 - 5 microns)	Good Dispersion (brown)	No Magneto-Optic Activity - Above 1%			
23				Perpendicular	1000						
24				Horizontal	1000						
25	Montedison (Italy) Acicular CrO ₂	Solvent Cast Acrylic Co-Polymer	30	No	-		Streaky Thin Film Tape Samples (2 - 5 microns)		Good Dispersion (black)	No Magneto-Optic Activity - Above 1%	
26				Perpendicular	1000						
27				Horizontal	1000						
28	Pierce-Wariner, Ground CoFe ₂ O ₄	Solvent Cast Acrylic Co-Polymer	30	No	-		Streaky Thin Film Tape Samples (2 - 5 microns)		Poor Dispersion (black)		No Magneto-Optic Activity - Above 1%
29				Horizontal	1000						
	Larger Particles										
30	Bayer BX12035/M Platelet Fe ₃ O ₄	Styrene	0.02	Yes	700	Polymer Block Samples	Optical Alignment and Particle Migration	No Magneto-Optic Activity - Above 1%			
31	BX12035/M	Styrene	0.12	Yes	1300		Optical Alignment				
32	BX12035/M	Styrene	0.025	Yes	1000		Larger Sample				
33	P.100 Iron Powder	Styrene	0.86	Yes	1000		Poor Dispersions formed Chains				
34	Hoganas (Sweden) Iron Powder ASC100-29	Styrene	0.86	Yes	1000						

TABLE 1 RESULTS (Continued)

4.4 Summary of Results

A wide range of magnetic particles were dispersed in a number of plastic matrices, principally polystyrene; the samples were sent to City of London Polytechnic for magneto-optic evaluation.

No intensity changes greater than about 1% were found for any specimens. Changes less than 1% were always attributable to either the coupling between the magnet and the photomultiplier or mechanical movement of the specimen toward a magnet pole face.

A 1% change corresponds to:

- a) a 1% change in the optical transmission of the specimen
- b) an optical phase difference of about 1 degree in the specimen
- c) a Faraday rotation of about 1 degree in the specimen

We believe that the samples were properly made, and that the negative result means that there is no large effect.

5. RECOMMENDATIONS

Although the majority of the samples prepared were well dispersed, and a wide range of particle shapes and sizes were examined, none of the samples exhibited a significant magneto-optic effect.

We believe that the loaded polymer samples were correctly made, and that most of the particle types were studied with some degree of alignment.

As none of the samples exhibited any significant magneto-optic effect, we conclude that there is no large effect in such suspensions of particles, and it is recommended that this approach to transparent magneto-optic devices is abandoned, unless there is interest in smaller effects.

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