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Formulation of an Invisible Infrared Printing Ink

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ABSTRACT

A new, invisible to the naked eye and infrared (IR) readable, ink formulation based on silicon(IV) 2,3-naphthalocyanine bis(trihexylsilyloxide) as colorant is described. The ink formulation is based on absorption and reflection of light in the IR, in contrast to the currently employed mechanism of excitation and fluorescence detection. The ink absorbs strongly at 790 nm and has highly transmitting characteristics in the visible. A good contrast level was obtained with an illumination source emitting at 790 nm. The ink is stable, lightfast and applicable to offset printing, and can also be extended to other printing techniques.

INTRODUCTION

Infrared absorbing dyes have numerous applications,[1,2] e.g. in optical recording systems, thermal writing displays, laser printers, laser filters, infrared photography, and bar code printing, as well as diverse applications in the medical field. In the case of invisible bar code printing, some of the existing devices exploit the process of fluorescence, in which a dye is excited by ultraviolet (UV), visible or near infrared (IR) radiation and the IR fluorescent light emitted by the dye substrate is detected.[3] In contrast, the present study describes an ink which uses the phenomena of absorption and reflection to detect otherwise invisible writing using infrared illumination and infrared detection. This eliminates the use of UV lamps or IR lasers for excitation, and instead appropriate IR light emitting diodes (LEDs) or filtered light from tungsten lamps can be used for illumination. Some of the existing invisible inks are formulated only for

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laser jet printing. In this study, the offset printing technique was chosen because it offers easy but high quality, high resolution printing in bulk quantities on a variety of surfaces in ordinarily required applications. In principle, the ink is not limited to any particular printing method and can be modified to suit the requirements of other printing techniques.

A printing ink is a mixture resulting from a coloring matter dispersed or dissolved in a vehicle or carrier. This mixture, in the form of a fluid or paste, can be printed on a substrate and dried. The colorants are organic or inorganic pigments, toners or dyes. The inks are usually categorized based on the mechanism of the particular printing process and the rheology of the ink. There are many types of lithographic inks, prepared to suit the press equipment and/or substrate of printing and applications.[4,6] The important requirements for a lithographic ink include no bleeding (transfer of coloring matter to the acidic fountain solution), no easy emulsification between ink and fountain solution, and a rheology compatible with the particular type of offset machine on which printing is done, e.g. sheet-fed or web-fed. The other requirements involve drying properties, and resistance to heat and light, etc. Thus, addition of a new material, such as a colorant, to a standard ink base is restricted so as not to alter any of these properties.

THE IR COLORANT

An IR ink must have high absorption in an IR region where light sources are available. In order to qualify as an invisible ink it should be transparent in the visible region. Further, the IR colorant to be used must be physically and chemically compatible with the ink base. With these requirements in view, many compounds were studied, among which silicon(IV) 2,3-naphthalocyanine bis(trihexyl-silyloxide) (SiNc), was found to be the most useful for this application; SiNc was purchased from Aldrich (Milwaukee, WI, USA). It was first synthesized by Wheeler *et al.*[7] in 1984, and is a green powder with a melting point of 278°C; it is stable and soluble in a variety of non-polar organic solvents. Originally SiNc was developed because of its possible applications in photodynamic sensitizers.[7–9] The structure of the compound is shown in Fig. 1. It consists of a π-conjugated naphthalocyanine ring with D_{4h} symmetry, Si being at the center and in the plane of the ring. The availability of two bonding electrons above and below the Nc plane allows the attachment of bulky substituents such as a trihexyl siloxyl group. Two $OSi(n\text{-}C_6H_{13})_3$ ligands are attached to the central Si atom, symmetrically and normal to the Nc plane in SiNc. The steric hindrance produced by the alkylsilyl

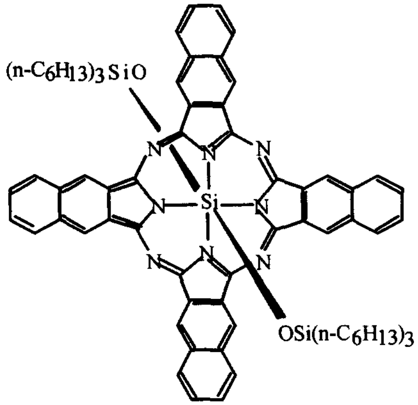

Fig. 1. Structure of silicon(IV) 2,3-naphthalocyanine bis(trihexyl-silyloxide).

groups as ligands helps in the solubility of the compound in various organic solvents. Many variations of the compound have been studied for various applications, such as optical recording media, organic photoconductors, and sensors.[10–13]

The spectra reported in the literature[7–9] were measured in solution form and exhibit the strongest Q-band absorption at 772 nm, other parts of the Q-band being an order of magnitude weaker in intensity. The Soret band lies in the region of 350 nm, and the absorption is less than 1% in the visible. Such spectral properties make this compound desirable for use as an IR colorant in an invisible IR readable printing ink.

EXPERIMENTAL

Tests for the compatibility of SiNc with the ingredients of the printing ink base were carried out. SiNc was mixed with the individual ingredients of the ink base, a film of the mixture was cast on a glass slide and the spectrum was measured from 400 nm to 820 nm. The spectral properties of SiNc were not affected by any of the ingredients of the standard ink base. Since fairly dispersed particles of sub-micron size are desirable for the printing process, the next stage involved proper dispersion of the colorant SiNc in the ink base, which also included breakdown of agglomerates.

The effective dispersion of SiNc was achieved by its initial wetting with a suitable surfactant; finely ground SiNc powder was mixed with the minimum quantity of cyclohexanone, just enough to wet the powder. Cyclohexanone was chosen because SiNc is fairly soluble in it, it is a relatively safe solvent, and its applications in ink formulation are known. After grinding, a small amount of linseed oil was added to make a

TABLE 1
A Typical Formulation for SiNc Invisible IR Readable Offset Printing Ink

Constituent	*Quantity*
Pigment (SiNc)	300 mg
Cyclohexanone	0·25 ml
Linseed oil	0·25 ml
Basic Pantone ink base	20 ml

paste of the pigment which was miscible with the ink base (vehicle). The agglomerates were then broken down to smaller sizes; on a large scale this is accomplished by grinding a sample in a roll mill or a ball mill, but grinding with a mortar and pestle yielded satisfactory results. The resulting paste was thoroughly mixed with the ink vehicle used in standard offset printing, purchased from Beacon (Somerville, MA, USA). A typical composition of the printing ink prepared for the present study is given in Table 1.

The thin films produced by lithographic printing on offset paper were studied for optical absorption and reflection properties. The reflection experiment was conducted by passing the light from a tungsten lamp through a chopper, and filtering it through a monochromator. It was then reflected from a printed paper, and detected by a Si detector connected to a lock-in amplifier. The monochromator (model H-20 from Instrument SA, Inc., Edison, NJ, USA) selected the wavelength with a bandpass of 2 nm. The absorption experiment was carried out by employing the same experimental setup mentioned above, and using films printed on transparent slides.

RESULTS AND DISCUSSION

The SiNc ink is dark green, and since the amount of SiNc colorant is very small compared with the ink base, various properties of the ink base such as viscosity are not significantly altered. Optical microscopy was used to determine the extent of dispersion. With the minimum detectable particle sizes of up to 0·5 μm, the size distribution could be qualitatively assessed by viewing a drop of ink placed on a clear glass slide and using a standard dispersion as a reference.

The molar absorption coefficient at the peak of the strongest Q-band absorption was calculated from a spectrum of SiNc in cyclohexanone and found to be $8{\cdot}5 \times 10^5$ l mol^{-1} cm^{-1}. The thickness of the printed film

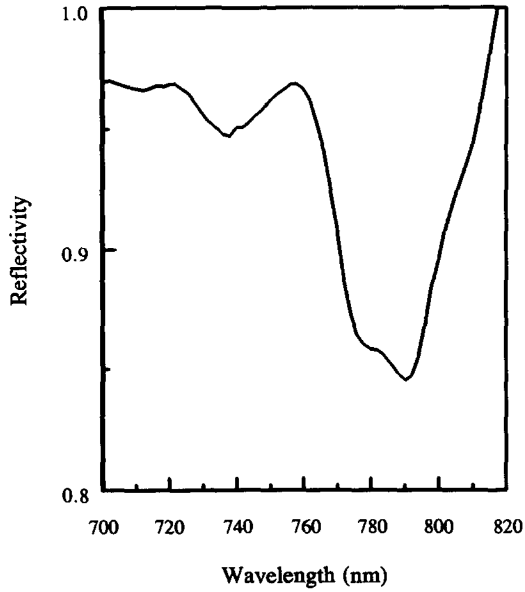

Fig. 2. Reflection from paper printed with invisible, IR readable ink as a function of wavelength.

was determined from the film deposited on a transparent slide, and was ca. 4 μm. The concentration of SiNc in the samples used for this study was ca. 15 mg ml^{-1}.

The reflection experiments on paper printed with the invisible IR readable printing ink were carried out as a function of wavelength. As shown in Fig. 2, the maximum absorption was determined to be at 790 nm. The transmission experiments with printed transparent slides show absorption at the same wavelength. The absorption maximum is red shifted and, as expected, considerably broadened in the thin film compared with the solution.

A small tint in the printout on white papers can be avoided or reduced by using a green tinted paper instead of white, using small amounts of other colorants, or by mixing a controlled amount of opaque white pigments (e.g. titanium oxide or zinc oxide) with the ink. The use of an opaque white pigment can diminish the contrast in the reading process by IR radiation, because they strongly reflect near IR light. Thus, the quantity of white pigment will be determined by the contrast requirements.

The characteristics of the SiNc invisible ink as related to its absorption and adhesion are found to be desirable. The choice of paper depends upon the particular application. The sunlight-fastness was checked by exposing a printed paper in sunlight for 12 h. Spectra measured before

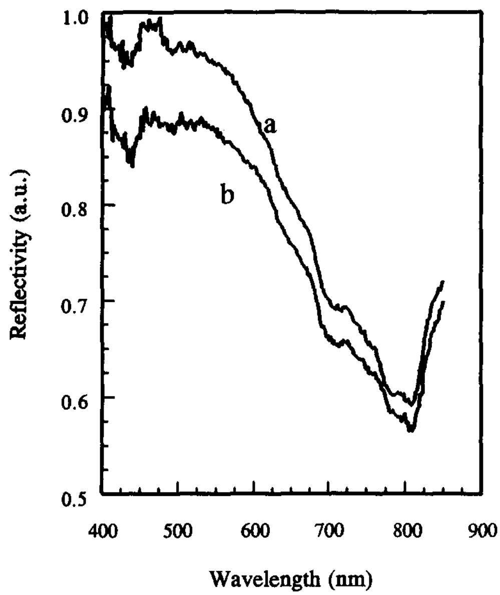

Fig. 3. Reflection from paper printed with invisible, IR readable ink as a function of wavelength. (a) Before exposure to sunlight, (b) after exposure to sunlight.

and after the exposure are presented in Fig. 3. A nominal change of less than 2% was detected in the infrared region. A slightly larger reduction in reflectivity in the visible region improves the invisibility, and is therefore beneficial.

CONCLUSION

A lithographic printing ink has been developed and tested successfully. The ink performs on the principle of absorption and reflection within the IR region. Material printed with this ink is invisible to the eye and can be read with the help of readily available light sources. Although the ink has been tested for offset printing techniques, it can easily be formulated for other printing techniques and surfaces.

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