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Improve Invisible Ink Production by the Europium Complexes

Mohammad AminEshraghi[1*], Mohammad Mahdi Tavana[1], Mohammad HassanEshraghi[2]

[1]Faculty of Medicine, Shahid Beheshti University of Medical Sciences, Tehran, Iran

[2]Department of Chemistry, Amin University of Police Sciences, Tehran, Iran

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Abstract

The invisible inks have many applications, including the use of banknote printing, code load, security documents and much of its application in the exchange of security information. Photoluminescence properties of lanthanide compounds that attracted the attention of many scholars in recent decades are one of the important factors in drying and fluidity of the ink. The solvent evaporation rate has a special importance in the formulation of resin systems. The solvent evaporation rate is often expressed in compare with a standard solvent evaporation rate, such as normal butylated acetate or ethyl ether. The mixing of some solvents may be used due to the formation of an azeotrope and the more rate of evaporation. In the formulation of the inks, the use of the weight ratio compared with the volume relationship has this advantage, which requires less mathematical calculations and operations, especially that this score is useful during the early stages of formulation. In this research, from 160 materials that were used, 11 items played a fundamental role, which were selected based on their formulation planned. The purpose of this research was to produce invisible ink.For this purpose, the relevant complexes were prepared, designed and the composition of the percentage of invisible ink was optimized. Eventually, obtainedresults were evaluated.

Keywords: *Evaporation Rate, Invisible Inks, Butyl Acetate.*

[*]***Corresponding author:****Mohammad Amin Eshraghi,Faculty of Medicine, Shahid Beheshti University of Medical Sciences, Tehran, Iran, E-mail: amineshragh@gmail.com.*

Introduction

When discussing the formulation of the ink, it is preferable to use weight percentages instead of the volumetric ratios of the pigments and accessory pigments; because the pigments and accessory pigments used in the ink have a wide specific weight spectrum. Knowing the pigments volume concentration (p.v.c) makes it possible to formulate and interpret the results of the final experiments with a more scientific view. Mineral pigments in solvents, resins and some of the oils are insoluble. The ability to dissolve organic pigments, in addition to the kind of pigments, depends on the nature and the amount of the group of segments present in their molecules, and because of this used derivatives of the ligands, they have been produced also with nitrate and sulfone. Because the size and the shape of the particles are those factors that often change with the pigments making procedure conditions, it is essential to control the different operations of the various constructions. Since the reaction temperature and the speed of stirring and even the size of the reaction vessel can change the pigment properties [1], after the sedimentation or non-solubilisation of the pigment is completed, it is filtered and dried, and finally the pigment is obtained from last levels.

The pigment has to be powdered and should be very careful in the drying process because most of the pigmentsare sensitive to heat, and some of them have a low melting pointand their very small particles tend to stick together in the heat. Excessive crushing may also cause damage to the pigments and the properties of the pigment. The pigment obtained from each reaction should be tested based on characteristics such as colour, fluorescence emission, resistance to light and chemical resistance. Because these pigments are used in offset printing, they should be hydrophobic. The gap between the excited triple levels of energy and the resonance levels of lanthanide must have a clear and distinct distance together [2-3].

Photoluminescenceproperties of the lanthanide compounds have attracted the attention of many scholars in recent decades [4-8]. One of the attractive aspects of lanthanide compounds is their line like emission, which leads to the high purity of the twinkling light [9-10]. The emission colour depends on the lanthanum ion and is independent of the surrounding environment. Most studies of these compounds are related to the inorganic compounds of lanthanides, such as β-Diketonate complexes[11-13]. For decades, to mineral-organic hybrids of lanthanides have been attracted many attentions. In these compounds, the molecular complexes of lanthanides, such as β-Diketonate lanthanide complex, is placed in a mineral environment as a host. The benefits of these compounds include the high potential of these compounds in various applications such as optical amplifiers, optical waveguides, OLEDs, etc. [14-15].The first use of the plastic as a preservative matrix by Wolf and colleagues reported, which they showed that the presence of the europium complex with 3 ligands: 4, 4,4 trifluoro-1- (2-thionyl) -1-3-buta-dien (TTFA), 4,4,4-trifluoro-1-(2-naphthyl)-1,3-

butanedione (NTFA) and solfo-4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (NTFA-SO3) in (poly methyl methacrylate) (PMMN)divulges laser activity. One of the most important properties of a pigment is the distribution of that pigment in the base color. The pigment distribution is carried out by various devices [16-17].Therefore, it is necessary to consider that how the ink is produced and this also should be a part of the formula. The small amount of diluent should be kept to use for regulating the viscosity of the ink in the mixture. This action reduces mistakes in adjusting the viscosity regulation. When the mixer is used for mixing, the stirring and mixing time play very important roles. Because too much stirring, foaming or blackening of ink was occuured.

A published article in 2014demonstrated that Europium and terbium trisdipicolinate complexes are inkjets printed onto paper with commercially available desktop inkjet printers. Together with a commercial blue luminescent ink, the red-emitting luminescent ink containing europium and the green-emitting luminescent ink containing terbium are used to reproduce accurate full-color images that are invisible under white light and appear under a 254 nm UV light. Such invisible luminescent images are attracted anti-counterfeiting security features. The luminescent prints have a color range (gamut) nearly as wide as the gamut of a standard RGB display [18]. Another article which was published in 2013 illustrates thatscreen printing fluorescent security inks can be widely applied in the field of anti-counterfeiting packaging and printing special. The paper-based screen printing fluorescence security ink was prepared by europium polymer fluorescent material as afluorescent agent. The performance of europium polymer was studied by IR, UV spectra; fluorescence spectra and fluorescent security performance of ink were studied by fluorescence spectrophotometer. The results showed that the fluorescence emission spectrum was narrow and had a main peak at 612nm with high fluorescence efficiency, so this ink had good fluorescence security performance [19].

Experimental

The complexes were prepared by Methanol-chloroform solutions and 1eq. of $Eu(NO_3)_3 \cdot 6H_2O$ with 1eq. of the TTFA, (TTFA- $NO_2)_3$ and NTFA-TPO ligands were mixed (Figure 1). Physical and spectroscopic data of the complexes are given below:

[TTFA-Eu]

m.p: 138-140 ° C. Yield 50% based on Eu. IR (KBr, cm^{-1}). 3112w (υ_{CH2}); 1655s ($\upsilon_{C=O}$); 1560 ($\upsilon_{C=C}$); 1384; 820; 720s.^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm): 93.5 (1C, s, CH_2); 109.78-126.02 (1C, m, CF_3); 128.04, 132.56, 135.2, 139.5 (4C, s, $C_{thiophene}$); 170.23-172.42 (1C, m, $C_{C=O}$ (CF_3)); 182.76 (1C, m, $C_{C=O}$ (Thiophene)). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm): 3.67 (2 H, s, CH_2); 5.7 (1H, s, $CH_{thiophene}$); 6.4 (1H, s, $CH_{thiophene}$); 7.4 (1H, s, $CH_{thiophene}$);UV-Vis spect (DMSO, 10^{-6} M): 275 nm.

[TTFA-NO_2-Eu]

m.p: 148-151 ° C. Yield 53% based on Eu. IR (KBr, cm^{-1}). 3184w (υ_{CH2}); 1678s ($\upsilon_{C=O}$); 1596 ($\upsilon_{C=C}$); 1580; 1388; 824; 720s.^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm): 93.68 (1C, s, CH_2); 109.65-126.15 (1C, m, CF_3); 129.32, 133.74, 136.12, 146.78 (4C, s, $C_{thiophene}$); 170.23-177.63 (1C, m, $C_{C=O}$ (CF_3)); 186.46 (1C, m, $C_{C=O}$ (Thiophene)). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm): 3.76 (2 H, s, CH_2); 7.11 (1H, s, $CH_{thiophene}$); 7.75 (1H, s, $CH_{thiophene}$); UV-Vis spect (DMSO, 10^{-6} M): 275 nm.

[NTFA-Eu]

m.p: 160-164° C. Yield59% based on Eu. IR (KBr, cm^{-1}). 3132w (υ_{CH2}); 1663s ($\upsilon_{C=O}$); 1577 ($\upsilon_{C=C}$); 1384; 822; 721s.^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm): 95.7 (1C, s, CH_2); 112.69-129.22 (1C, m, CF_3); 128.41-138.63 (10C, $C_{aromatic}$); 170.23-175.65 (1C, m, $C_{C=O}$ (CF_3)); 184.33 (1C, m, $C_{C=O}$ (Aromatic)). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm): 3.11 (2 H, s, CH_2); 7.3-8.24 (7H, s, $CH_{aromatic}$); UV-Vis spect (DMSO, 10^{-6} M): 345, 266 nm.

Tests performed to record emission spectra

Firstly, the solution of commercial complexes with the same concentration of10^{-6} M in methanol solvent was exposed to radiation of different wavelengths and their emission intensity was determined to obtain the best excitation wavelength.

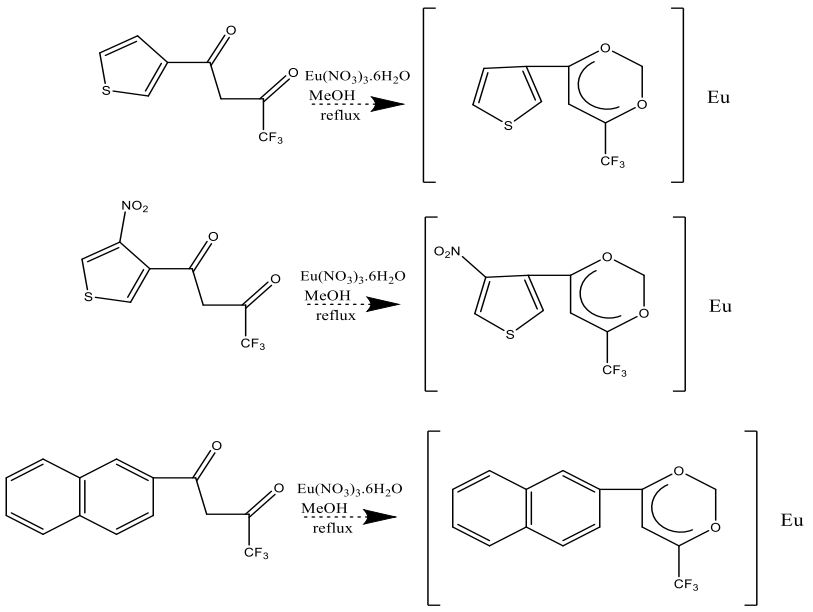

Figure 1. Formulation of studied complexes.

Then, the wavelength of 390 nm continuously and repeatedly was shined to the solution of various complexes and their emission spectra were recorded. In the reported spectra, the peak in 390 nm

belongs toλ_{ex}. The obtained results were evaluated and compared and the synthesized complexes were found to have fluorescence emission.

Results and discussion

In this research, 160 materials were used, 11 items played a major role were selected and formulated. The formulation was prepared and presented in the table below (Table 1).

Table 1. Combinations and weights of materials.

Combination	Weights of materials
Linseed oil	10mg
Phthalic anhydride	5mg
Talc powder	2mg
Kaolin	2mg
Normal butanol	3mg
Aerosil	15mg
Paraffin	15mg
Petroleum resin	15mg
Camphor	10mg
Petroleum	8mg
B-Diketonate complex	3mg

As shown below in Table 2, in this series of tests, all materials were kept constant and only petroleum related quantities were changed during the 5 test series. As explained in column 3, the optimum amounts of 5 g were selected for petroleum.

Table 2. Formulation designed to find the optimal amount of petroleum.

Substituted material	Test1	Test2	Test3	Test4	Test5
Petroleum(mg)	7	8	5	13	15

In this series of tests all the materials have been fixed and only the quantities related to the petroleum resin have been changed during the 5 series of experiments. As in Step 3, the optimal 10 g amounts for the petroleum resin were selected. In addition, the selected resin is completely colorless and is made from Merck Co., and these resins are completely special so that, under the visible light, after combining with the europium, it does not reflect any color. The resins are in different sizes, so that no matter how much its size be smaller, its solubility in oil is better. See table below (Table 3).

Table 3. Formulation designed to find the optimal amount of petroleum resin.

Substituted material	Test1	Test2	Test 3	Test4	Test5
Petroleum resin (mg)	7	8	10	13	16

In this series of tests, all the materials have been fixed and only the amounts associated with the 5 series of the test have been altered. As can be seen, column 2 of the optimum amount of 5 mg for the β-diketonate complex Lanthanide was selected, as shown in Table 4.

Table 4. Formulation designed to find the optimal amount of β-diketonate lanthanide. Complexes.

Substituted material	Test1	Test2	Test3	Test4	Test5
β-diketonate (mg)	3	5	6	7	8

In this series of tests all the materials have been fixed and only the amounts related to aerosil have been changed during the 5 series of experiments. As it was done, column 3 of the optimum value of 15 grams was chosen for Aerosil (Table 5).

Table 5. Formulation designed to find the optimal amount of aerosil complexes.

Substituted material	Test1	Test2	Test3	Test4	Test5
Aerosil(mg)	9	10	15	17	20

In this series of tests, all the materials have been fixed and only paraffin-related amounts have changed over the five test series. As you can see in Table 6, Column 2 has the optimal particle amount of 15 mg.

Table 6. Formulation designed to find the optimal paraffin amount. (Petroleum solvent).

Substituted material	Test1	Test2	Test3	Test4	Test5
Paraffin(mg)	8	15	16	17	20

In this series of tests, all materials were fixed and only the amounts related to phthalic anhydride were changed during the 5 test series. As can be seen in table 7, column 2 was selected for optimal 3 mg for phthalic anhydride.

Table 7. Formulation designed to find the optimal amount of phthalic anhydride.

Substituted material	Test1	Test2	Test3	Test4	Test5
phthalic anhydride(mg)	10	3	12	7	8

In this series of tests, all the materials have been fixed and only the related quantities of talc powder have been changed in the 5 series of experiments. As can be seen in table 8, column 1, the optimal values of 1 mg for talc powder was selected.

Table 8. Formulation designed to find the optimal amount of talc powder.

Substituted material	Test1	Test2	Test3	Test4	Test5
Talc powder(mg)	1	3	5	8	10

In this series of tests, all the materials have been fixed and only the quantities related to kaolin have been changed during the 5 test series. As in column 1, the optimal amounts of 1 mg for kaolin were selected. See table 9.

Table 9. Formulation designed to find the optimal amount of kaolin. petrolumpepetroleum

Substituted material	Test1	Test2	Test3	Test4	Test5
Kaolin(mg)	1	3	5	8	10

In this series of tests, all the materials were fixed and only the amounts related to the linseed oil were changed in the 5 series of experiments. As shown in Table 10, column No. 3 was chosen as the optimum amount of 10 mg for linseed oil.

Table 10. Formulation designed to find the optimal amount of linseed oil.

Substituted material	Test1	Test2	Test3	Test4	Test5
Linseed oil(mg)	10	15	12	28	35

In this series of tests, all the materials have been fixed and only the amounts related to camphor have been changed in the 5 series of experiments. As in Step 3, column 8 of the optimal amount of 8 mg was selected (Table 11).

Table 11. Formulation designed to find the optimal amount of camphor (petroleum solvent).

Substituted material	Test1	Test2	Test3	Test4	Test5
Camphor(mg)	3	5	8	10	15

In this series of tests, all of the materials have been fixed and only the amounts associated with normal butanol have been changed during the 5 series of experiments. As can be seen in table 12, in column 1, optimal amounts of 1 mg for normal butanol were selected.

Table 12. Formulation designed to find the optimal amount of camphor.

Substituted material	Test1	Test2	Test3	Test4	Test5
Normal butanol(mg)	1	3	6	8	10

For the production of invisible ink, considering that the percentage of its constituents has been confirmed, its manufacture at higher scales was used for use in the security offset printing machine, that the percentage of components shown in the table below (Table 13).

Table13. Percentage of components for invisible ink production.

Combination	Weight percentage
Linseed oil	0/033
Phthalic anhydrid	0/169
Talc powder	0/0067
Kaolin	0/0067
Normal butanol	0/0107
Aerosil	0/0508
Paraffin	0/0508
Petroleum resin	0/508
Camphor	0/033
Petroleum	0/270
β-diketonate	0/107

Conclusion

In this study, four complexes were synthesized as pigments, using the europium and two ligands of ß-Diketonate and related derivatives. The fluorescence of invisible ink in security offset was prepared using a new formulation. This technology has been provided by some intelligence services of specific countries and many researchers in our country have been involved in their procurement, which were not successful. In this research, we were able to achieve the technology of making such inks, and hope the researchers continue this way and produce other types of this ink, such as dual security inks- multiple security inks - biometric inks and etc. in different colors, which have widelyused insecurity systems - banknote Printing - barcodes - stamp sensors and etc.

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