Original Paper

Solid-Solid Separation of Fluorescent Powders by Liquid-Liquid Extraction Using Aqueous and Organic Phases

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Abstract

Two-step liquid-liquid extraction methods using aqueous and organic phases for separation of red (Y_2O_3 : Eu^{3+}), blue ($\text{BaMgAl}_{10}\text{O}_{17}$: Eu^{2+}) and green ($\text{CeMgAl}_{10}\text{O}_{17}$: Tb^{3+}) fine fluorescent powders were proposed in this paper. At first, the blue powder was extracted selectively into heptane phase using a chelating agent, 2-thenoyltrifluoroacetone (HTTA, $\text{CF}_3\text{COCH}_2\text{COC}_4\text{H}_9\text{S}$) under alkaline pH condition. Then, chloroform was used for extracting the green powder into the chloroform phase. The red powder separating from the green powder remained in aqueous phase with a depressant, potassium sodium tartrate tetrahydrate (PST, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$). The powders could be well separated in terms of their grade and recovery. The results suggested directions for future research into the recycling of fluorescent powders from fluorescent lights.

Key words: liquid-liquid extraction, fluorescent powder, separation, recycle, waste

1. Introduction

Proper handling and disposal of used fluorescent lights become an increasingly expensive and problematic chore for big users of these lights. Recycling is a viable option, which can reduce the risk of future financial liability associated with hazardous waste.

After being crushed under a closed system, lamp materials are separated into four waste streams; aluminum and brass end caps, glass, mercury, and fluorescent powders. The metals, glass and mercury can be classified and purified by magnetic separation and triple distillation for recycling of these materials. However, the collected fluorescent powder complex cannot be further separated and reused to make new lamps.

At previous research work, yttrium and europium elements could be recovered from waste fluorescent powder sludge by means of leaching treat-

ment and oxalate precipitation method after pneumatic classification¹⁾. Then, red fluorescent powder (Y_2O_3 : Eu^{3+}) was reproduced by co-precipitation process²⁾. However, some disadvantages exist on this process due to the long treatment process and expensive cost.

Our research purpose is to propose a new method to separate artificial mixture of red, blue and green fluorescent powders from their artificial mixture, aiming the recycling of these valuable and limited secondary rare earth resources conveniently. It is not suitable to conduct separation of the fluorescent powders by floatation or other conventional mineral processing techniques because particle size of the fluorescent powders is very fine (the average grain size is under $5\text{ }\mu\text{m}$)³⁾. Also other physical properties of fluorescent powders, such as specific gravity and zeta potential are quite similar. Therefore, liquid-liquid extraction has been chosen to conduct solid-solid separation of the fluorescent powders from their artificial mixture. The extraction has achieved high recovery

Table 1 The chemical compositions of pure three kinds of fluorescent powder samples.

Color (Formula)	Element Content (%)							
	O	Y	Eu	Al	Mg	Ba	Ce	Tb
Red (Y_2O_3 ; Eu^{3+})	17.5	67.2	6.5					
Green ($\text{CeMgAl}_{10}\text{O}_{17}$; Tb^{3+})	42.6			31.3	5.7		9.5	5.3
Blue ($\text{BaMgAl}_{10}\text{O}_{17}$; Eu^{2+})	42.3		1.9	32.4	2.7	12.4		

(Red: 94.1%; Green: 76.0%; Blue: 98.7%) and grade (Red: 96.9%; Green: 94.6%; Blue: 74.1%) of fluorescent powders. The result provides a new possibility for the recycling of fluorescent powder sludge from used fluorescent lights in the near future.

2. Experimental

2.1 Fluorescent powders

Table 1 shows the chemical compositions of pure fluorescent powder samples analyzed by ICP-AES (Seiko Instruments Inc., SPS 3000). Before analysis by ICP-AES, samples should be roasted and smelted with appropriate amount of sodium carbonate and H_3BO_3 at 1100–1200°C for 20–30 minutes, and then dissolved using 1 : 1 HCl solution. The pure samples are commercial fluorescent powder products which have been widely applied to fluorescent lights and low voltage displays. The powders contained variety of rare earth metals, such as yttrium, europium and cerium. Measurement of zeta potential and particle size distribution of fluorescent powders are investigated using Electrophoretic Light Scattering Spectrophotometer (Otsuka Electronics Co.Ltd., ELS8000). The results of zeta potential measurement are shown in Fig. 1. The fluorescent powders in aqueous solution exhibited negative zeta potential at the pH values from 2 to 12. Particle size of the fluorescent powders was in the range from 1 to 10 μm , and the average particle size was under 5 μm . The measurement of specific gravity of the fluorescent powders was conducted using a pycnometer. The measured specific gravities of the red, green and blue fluorescent powders were 4.30, 4.06 and 3.51, respectively.

2.2 Chemical reagents

Potassium sodium tartrate tetrahydrate (PST, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) of analytical grade, 2-Thenoyltrifluoroacetone (HTTA, $\text{CF}_3\text{COCH}_2\text{CO}-\text{C}_4\text{H}_3\text{S}$) of the purity over 98%, 1-pentanol, chloroform, and heptane were used. HCl, NaOH, and Na_2CO_3 were used to adjust the pH value of aqueous phase.

Fig. 1 Zeta potential of three kinds of fluorescent powder powders. **Fig. 2** Flow sheet 1 for separation of artificial mixture of fluorescent powders.

2.3 Extraction and separation of tricolor fluorescent powders

Two types of flow sheet for separating three kinds of fluorescent powders were proposed in this research work. Flow sheet 1 for separating fluorescent powders was shown in Fig. 2. Prior to

the extraction, the three kinds of fluorescent powders, i.e. red, green and blue were mixed. Surfactants, PST and HTTA, were dissolved in aqueous and heptane phases, respectively, by ultrasonic-wave. The pH of the aqueous phase was adjusted by using Na_2CO_3 or NaOH . After the fluorescent powders were mixed with the aqueous phase, and shaken for 1–2 min, heptane phase was mixed with the aqueous phase containing the fluorescent powders. The volumetric ratio of heptane and aqueous phase was maintained 2 : 3. The solution consisting two phases was shaken at room temperature for 5 min. The blue powder was extracted into the upper phase (heptane). The green and red powders remained in the lower phase (aqueous). The green-red mixture was washed by 99.5% ethanol to remove HTTA attached on the powders. A second extraction for the remaining powders was conducted using two phases, chloroform containing 1-pentanol as a stabilizer of oil droplet and aqueous containing dissolved PST as a depressant. After the green-red mixture was mixed with the chloroform phase, and shaken for 1 to 2 minutes, aqueous phase was mixed with the chloroform phase containing the green-red mixture. The volumetric ratio of chloroform and aqueous phase was maintained from 1 : 1 to 1 : 5. The solution consisting two phases was shaken at room temperature for 5 min. The green powder was then extracted into chloroform phase and separated from the red powder, which remained in the aqueous phase. Sample powders collected at each step were analyzed using ICP-AES after dissolution of the powders with HClO_4 and HNO_3 as well as dissolving them with aqua regia ($\text{HNO}_3 : \text{HCl} = 1 : 3$).

Flow sheet 2 for separating three kinds of fluorescent powders is shown in Fig. 3. Prior to the extraction, the three kinds of fluorescent powders, i.e. red, green and blue were mixed. A depressant PST was dissolved in aqueous phase, by ultrasonic-wave. After the fluorescent powders were mixed with the chloroform phase containing 1-pentanol, and shaken for 1 to 2 minutes, aqueous phase was mixed with the chloroform phase containing the fluorescent powders. The volumetric ratio of heptane and aqueous phase was maintained 2 : 3. The solution consisting two phases was shaken at room temperature for 5 min. The red powder was extracted into the upper phase (aqueous). The green and blue powders remained in the lower phase (chloroform). The green-red mixture was washed by 99.5% ethanol and deionized water to remove PST attached on the powders. A second extraction for the remaining powders was conducted using two phases, aqueous phase con-

Fig. 3 Flow sheet 2 for separation of artificial mixture of fluorescent powders.

taining dissolved PST as an emulsifying agent and heptane phase containing dissolved HTTA as a chelate agent. After the green-blue mixture was mixed with the aqueous phase, and shaken for 1 to 2 minutes, heptane phase was mixed with the aqueous phase containing the green-blue mixture. The volumetric ratio of heptane and aqueous phase was maintained from 1 : 1 to 1 : 5. The solution consisting two phases was shaken at room temperature for 5 min. The blue powder was then extracted into heptane phase and separated from the green powder, which remained in the aqueous phase. Sample powders collected at each step were analyzed using ICP-AES after dissolution of the powders with HClO_4 and HNO_3 as well as dissolving them with aqua regia ($\text{HNO}_3 : \text{HCl} = 1 : 3$).

2.4 Evaluation of each extraction step

To optimize experimental conditions at each extraction step for separating artificial mixture of fluorescent powders, Efficiency was used⁴⁾:

$$\text{Efficiency} = \left[\left(\frac{M_{a(1)}}{M_{a(i)}} \right) \times \left(\frac{M_{a(1)}}{M_1} \right) \right] \times 100[\%] \quad (1)$$

where $M_{a(1)}$ was the mass of material "a" in output stream 1; $M_{a(i)}$ was the mass of materials "a" in feed; M_1 was the mass of the output stream 1.

2.5 Evaluation of two flow sheets

Considering the separation of artificial mixture of fluorescent powders, where all compounds of the mixture to be separated were valuable, the authors have modified the Doddiba's definition⁴⁾ as

follows:

$$\begin{aligned} \text{Efficiency} &= \left[\left(\frac{M_{a(1)}}{M_{a(i)}} \right) \times \left(\frac{M_{a(1)}}{M_1} \right) \right] \times \left[\left(\frac{M_{b(2)}}{M_{b(i)}} \right) \times \left(\frac{M_{b(2)}}{M_2} \right) \right] \\ &\times \left[\left(\frac{M_{c(3)}}{M_{c(i)}} \right) \times \left(\frac{M_{c(3)}}{M_3} \right) \right] \times \dots \times \left[\left(\frac{M_{x(n)}}{M_{x(i)}} \right) \times \left(\frac{M_{x(n)}}{M_n} \right) \right] \\ &\times 100[\%] \end{aligned} \quad (2)$$

where $M_{a(1)}$ was the mass of material “a” in output stream 1; $M_{a(i)}$ was the mass of materials “a” in feed; M_1 was the mass of the output stream 1; $M_{b(2)}$ was the mass of the material “b” in output stream 2, $M_{b(i)}$ was the mass of materials “b” in feed; M_2 was the mass of the output stream 2; $M_{c(3)}$ was the mass of the material “c” in output stream 3, $M_{c(i)}$ was the mass of materials “c” in feed; M_3 was the mass of the output stream 3; $M_{x(n)}$ was the mass of the material “x” in output stream n, $M_{x(i)}$ was the mass of materials “x” in feed; M_n was the mass of the output stream n. It can be noted that Eq. 2 incorporates both fractions of the grade ($M_{x(n)}/M_n$) and recovery ($M_{x(n)}/M_{x(i)}$) of separated products. Equation 2 was used to evaluate efficiency of two types of flow sheet (flow sheets 1 and 2).

3. Results and discussion

3.1 Separation of three kinds of fluorescent powder from artificial mixture of fluorescent powders following the flow sheet 1

In flow sheet 1, effect of pH values of aqueous phase, concentration of 1-pentanol and concentration of Na_2CO_3 on separation results of the fluorescent powders were observed. At first effect of pH values of aqueous phase was observed (Fig. 4). The blue fluorescent powder extracted into heptane phase selectively in the pH range from 7 to 11. The red and green powders almost cannot be extracted into heptane phase in this pH range. The best extraction rate of the blue fluorescent powder to heptane phase is almost 100% when pH value of the aqueous phase is approximately 10. As shown in Fig. 1, there is a significant difference among the zeta potential values of three fluorescent powders at this point; absolute value of zeta potential of the blue fluorescent powder at pH 10 (−17mV) is quite smaller than that of the others (Red: −40mV, Green: −45mV) at pH 10. Therefore, the blue powder has the higher possibility of aggregation than the other powders by adsorbing cationic ion. Here, concentration of HTTA species, [HTTA] and $[\text{TTA}^-]$, as well as $[\text{OH}^-]$, which is abundant in aqueous solution at a certain pH range was calculated, as a function of pH values of

Fig. 4 Effect of pH values of the aqueous phase on the extraction of the fluorescent powders to the heptane phase at first extraction step of the flow sheet 1. (Experimental conditions: 1% HTTA in heptane, 1% PST in aqueous phase, organic/aqueous ratio 1/3)

aqueous solution. The following reaction was occurred inside the solution containing total concentration of HTTA of C_a :

$$K_a = \frac{[\text{H}^+][\text{TTA}^-]}{[\text{HTTA}]} = 7.94 \times 10^{-10.5} \quad (4)$$

Figure 5 shows the calculation results of concentration of HTTA species and hydroxyl ion as a function of pH values. Lower than pH8, the amount of reactive HTTA species, TTA^- was quite smaller than the amount of non-reactive HTTA species, HTTA. The blue powder containing Al^{3+} ion and Ba^{2+} ion on its surface was not strongly attracted by TTA^- due to the low concentration of TTA^- and was not obtained flotability. Higher than pH8, TTA^- , which was reactive to Al^{3+} ion and Ba^{2+} ion of the blue powder, was abundant in the solution. This in turn led to high flotability of the blue powder. Especially, Ba^{2+} ion, which would be most abundant ion dissociated from the blue powder, was reactive to the TTA^- at higher than pH8 and made the surface of the blue powder hydrophobic. Measurement of electric conductivity of aqueous solution containing HTTA at pH 10 as a function of Al^{3+} ion and Ba^{2+} ion concentration was conducted to observe the formation of insoluble salt of TTA^- with Al^{3+} ion and Ba^{2+} ion (Fig. 6). The solution pH was adjusted to be 10, which was the optimum pH of the aqueous phase on the extraction of the fluorescent

Fig. 5 Concentration of HTTA species and hydroxyl ion as a function of pH values of aqueous solution.

Fig. 6 Relationship between electric conductivity of the aqueous solution containing 10^{-5} mol/L of HTTA as a function of Al^{3+} ion or Ba^{2+} ion concentration (Experimental conditions: pH 10 of aqueous solution).

powders to the heptane phase at first extraction step of the flow sheet 1 (Fig. 4). Figure 6 showed that both Al^{3+} ion and Ba^{2+} ion was formed insoluble salt with TTA^- because electric conductivity decreased until the certain point (Al^{3+} concentration: 6.0×10^{-6} mol/L; Ba^{2+} concentration: 8.0×10^{-6} mol/L) and then increased. Before the point, about 1×10^{-6} mol/L of TTA^- formed insoluble salt with Al^{3+} ion or Ba^{2+} ion, and the formation of insoluble salt decreased the electric conductivity. At the point, though some amount of Al^{3+} ion or Ba^{2+} ion changed to $\text{Al}(\text{OH})_3$ ($K_{\text{sp}} = 4.6 \times 10^{-33}$)⁶⁾ and $\text{Ba}(\text{OH})_2$ ($K_{\text{sp}} = 9.7 \times 10^{-4}$)⁷⁾, the number of electron of TTA^- and the number of proton of Al^{3+} ion or

Fig. 7 Effect of concentration of 1-pentanol on the extraction of blue powder to the heptane phase at first extraction step of the flow sheet 1. (Experimental conditions: PST 1% in aqueous phase, pH 10.3 of aqueous phase, 0.25% HTTA in heptane)

Ba^{2+} ion were almost balanced. Therefore, decreasing the electric conductivity was stopped. After the point, TTA^- could not form insoluble salt with Al^{3+} ion or Ba^{2+} ion due to existence of few TAA^- other than insoluble salt in the aqueous solution, and the excess Al^{3+} ion or Ba^{2+} ion increased the electric conductivity. Higher than pH 11, hydroxyl ion was abundant in the aqueous solution, which competed with TTA^- to react with Ba^{2+} ion. The competitive adsorption limited the flotability of the blue powder to the heptane phase, which decreased the extraction rate of the blue powder at pHs higher than 11.

Secondly, effect of concentration of 1-pentanol on blue fluorescent powder extraction has been observed. (Fig. 7) It was found that 1-pentanol is sensitive to the separation of the fluorescent powders and the best result has been achieved using 0.05% of 1-pentanol at efficiency of 82.8%. 1-Pentanol was acted as a stabilizer, which stabilized the heptane droplet dissolved inside the aqueous phase because hydroxyl ion of 1-pentanol was attractive to the water molecule while hydrocarbon group of 1-pentanol was reactive to the heptane molecule. At higher concentration of 1-pentanol, grade and recovery of the blue powder decreased to 77.2% and 88.4%, respectively. The stability of heptane droplets was increased with increasing the amount of 1-pentanol added. Increasing the stability of the heptane droplets contributed to excess heptane particles in the aqueous phase

Fig. 8 Effect of concentration of Na₂CO₃ on extraction of the blue powder to the heptane phase at first extraction step of the flow sheet 1. (Experimental conditions: 0.25% HTTA in heptane phase, 1% PST in aqueous phase, organic/aqueous ratio 2/3, pH 10.3)

effectively colliding heptane particle from accessing the red and green powders as well as blue powder, which was supposed to be attracted with heptane droplets and object to be moved towards the heptane-aqueous interface. Therefore, increasing the amount of 1-pentanol concentration increased the amount of red and green powders moved to the heptane-aqueous interface, and led to decrease the grade and recovery of the blue powder to the heptane-aqueous interface.

Thirdly, effect of concentration of Na₂CO₃ on blue fluorescent powder extraction has been observed. (Fig. 8) As a buffer solution, appropriate amount of Na₂CO₃ is very important to stabilize pH condition of the aqueous solution. The carbonate ion, CO₃²⁻, was much stronger base ($K_b = 1.8 \times 10^{-4}$) than the HCO₃⁻ ion ($K_b = 2.3 \times 10^{-8}$)⁸⁾ and would strongly maintain pH value of the solution should that be critical for extracted materials' stabilization. When the concentration of Na₂CO₃ was from 0.03% to 0.158%, pH value of aqueous solution kept stable around 10.3. However, results of extraction and separation of the blue fluorescent powder has changed slightly at various concentration of Na₂CO₃. The reasonable concentration of Na₂CO₃ was 0.058%. The effect of Na₂CO₃ concentration on pH values of aqueous solution, which varied the concentration of HTTA species. Calculation of pH values at a various Na₂CO₃ con-

centration was conducted using following steps:

$$\frac{[H^+][A^{2-}]}{[HA^-]} = K_{a2} = 6 \times 10^{-11} \quad (5)$$

where A is acid, K_{a2} is second acid dissociation constant of Na₂CO₃. Assuming that total concentration of Na₂CO₃ is C and generation rate of HA⁻ is α , the following relationships was comprised:

$$[A^{2-}] = C(1-\alpha), [HA^-] = C\alpha, [OH^-] \approx C\alpha \quad (6)$$

Formation reaction was described below:

Then, first base dissociation constant (K_{b1}) was described below:

$$\frac{[HA^-][OH^-]}{[A^{2-}]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = K_{b1} = \frac{K_w}{K_{a2}} \quad (8)$$

$$\alpha = \frac{-K_w + \sqrt{K_w^2 + 4CK_{a2}K_w}}{2CK_{a2}} \quad (9)$$

$$[OH^-] = C\alpha \quad (10)$$

$$pOH = -\log[OH^-] \quad (11)$$

$$pH = K_w - pOH \quad (12)$$

where K_w is dissociation constant of water. By solving Eqs. (5), (9)–(12), experimental pH values of aqueous solution at 0.03%, 0.058%, 0.111% and 0.158% of Na₂CO₃ were calculated as 10.8, 11.0, 11.1 and 11.2, respectively. pH values of aqueous solution affected the concentration of HTTA species and hydroxyl ion as a function of pH values of aqueous solution (Fig. 5). Lower than pH 11, the recovery of the blue powder containing Ba²⁺ ion using a chelating agent, HTTA was successfully conducted due to the considerably low concentration of hydroxyl ion. Higher than pH 11, concentration of hydroxyl ion was gradually increased, which competed with TTA⁻ to attract with Ba²⁺ ion. The competitive adsorption limited the flotability of the blue powder to the heptane phase, which decreased the recovery and grade of the blue powder.

3.2 Separation of red fluorescent powder from artificial mixture of fluorescent powder following flow sheet 2 (First extraction step)

In the first step of the flow sheet 2, pH values of aqueous solution, PST concentration, concentration of 1-pentanol, solid/liquid ratio, numbers of extraction process repeated have been investigated. Figure 9 shows effect of pH values of aqueous phase on the extraction of the fluorescent powders to the aqueous phase at first extraction step of the flow sheet 2. The blue and green powders were ex-

Fig. 9 Effect of pH values of the aqueous phase on extraction of the fluorescent powders to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: 0.05% PST in aqueous phase, organic/aqueous ratio 2/3)

tracted into chloroform phase because chloroform was a heavy solvent, which was widely used for extracting metal complex from chloroform phase as diluent¹⁰. The extraction rate of the blue and green powders to the chloroform phase were approximately 90% in the pH range from 7 to 11, while the red fluorescent powder dispersed in the aqueous phase and the recovery of the red powder to the chloroform phase was less than 10%. The following reaction was occurred inside the solution containing total concentration of PST (RCOOH_2) of C_a :

$$K_{a1} = \frac{[\text{H}^+][\text{RCOOH}^-]}{[\text{RCOOH}_2]} = 9.12 \times 10^{-4} \quad (14)$$

$$K_{a2} = \frac{[\text{H}^+][\text{RCOO}^{2-}]}{[\text{RCOOH}^-]} = 4.27 \times 10^{-5} \quad (16)$$

Total concentration of RCOOH_2 , RCOOH^- and RCOO^{2-} was equal to the concentration of C_a :

$$C_a = [\text{RCOOH}_2] + [\text{RCOOH}^-] + [\text{RCOO}^{2-}] \quad (17)$$

K_{a1} and K_{a2} were used to convert the each PST species described by K_{a1} , K_{a2} , C_a and $[\text{H}^+]$:

$$C_a = \left\{ \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} + \frac{[\text{H}^+]}{K_{a2}} + 1 \right\} [\text{RCOO}^{2-}] \quad (18)$$

Fig. 10 Concentration of PST species as a function of pH values of aqueous solution.

Then, arrangement was made to describe $[\text{RCOO}^{2-}]$, $[\text{RCOOH}^-]$ and $[\text{RCOOH}_2]$:

$$[\text{RCOO}^{2-}] = \frac{C_a K_{a1} K_{a2}}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}} \quad (19)$$

$$[\text{RCOOH}^-] = \frac{C_a [\text{H}^+] K_{a1}}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}} \quad (20)$$

$$[\text{RCOOH}_2] = \frac{C_a [\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}} \quad (21)$$

Concentration of PST species, $[\text{RCOO}^{2-}]$, $[\text{RCOOH}^-]$ and $[\text{RCOOH}_2]$, as a function of pH values of aqueous solution, was calculated by using Eqs. (19)–(21). Figure 10 shows the calculation results of the relationship between pH values and concentration of PST species. Lower than pH 6, reactive PST species, RCOO^{2-} was smaller than non-reactive PST species, RCOOH_2 . Y^{3+} ion of the red powder was not strongly attracted by RCOO^{2-} of PST and did not lose mobility. Higher than pH 6, RCOO^{2-} was abundant in the solution, which was reactive to Y^{3+} ion of the red powder. Higher than pH 10, hydroxyl ion was abundant in the aqueous solution, which competed with RCOO^{2-} to attract with Y^{3+} . The competitive adsorption kept the mobility of the red powder to the chloroform phase, which minimized the difference of the extraction rate of the both powders at pH 7 to 11.

The effect of pH value of aqueous phase on the extraction of the red powder to the aqueous phase at first extraction step of flow sheet 2 is shown in Fig. 11. Suitable pH range is between 7 and 11.

Fig. 11 Effect of pH of aqueous phase on extraction of the red fluorescent powder to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: 0.5% PST in aqueous phase, solid/liquid ratio 30 g/L, organic/aqueous ratio 2/3, 1-pentanol/chloroform ratio 1/4)

Fig. 12 Effect of PST concentration on extraction of the red fluorescent powder to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: solid/liquid ratio 30 g/L, organic/aqueous ratio 2/3, 1-pentanol/chloroform ratio 1/4, pH 7 of aqueous phase)

Especially, the grade and recovery of blue product are over 90% at pH 7.8. As shown in Fig. 10, lower than pH 6, reactive PST species, RCOOH^- and RCOO^{2-} were smaller than non-reactive PST species, RCOOH_2 . Y^{3+} ion of the red powder was not strongly attracted by ester group (RCOOH^- and RCOO^{2-}) of PST and did not lose mobility. Higher than pH 6, RCOO^{2-} was abundant in the solution, which was reactive to Y^{3+} ion of the red powder.

Fig. 13 Electric conductivity of aqueous solution at pH 7 as a function of PST concentration.

Higher than pH 10, hydroxyl ion was abundant in the solution, which competed with RCOO^{2-} to attract with Y^{3+} ion. The competitive adsorption limited the mobility of the red powder to the chloroform phase, which lowered the grade of the red powder to the aqueous phase at pH 8 to 11.

The effect of PST concentration on the fluorescent powders was observed. At this time, PST depressed the red fluorescent powder with a good selectivity, and the appropriate concentration of PST is also investigated (Fig. 12). Appropriate concentration of PST is from 0.4% to 0.8%. Efficiency of the extractions is 84.8% and 85.0%. Without PST depressant, the red fluorescent powder cannot be separated well from the other powders. At higher concentration of PST, grade of the red powder dropped to 73.5% and 91.8%. This trend may be attributed by excess PST particles in the aqueous phase effectively collide the red powder and other green and blue powders. Measurement of electric conductivity of aqueous solution at pH 7 as a function of PST concentration was conducted to observe the critical micelle concentration of PST (Fig. 13). Bending point of the graph was observed at PST concentration of 0.8%. Lower than PST concentration of 0.8%, free reactive PST species, RCOOH^- and RCOO^{2-} , which reacted with the red powder, were abundant. Higher than PST concentration of 0.8%, RCOOH^- and RCOO^{2-} started micelle formation and the concentration of these PST species were gradually decreasing. Therefore, effect of PST on depressing the red powder at PST concentration of below 0.8% was lower than the effect at PST concentration of higher than 0.8%. Less effect of PST on depressing the red powder decreased the grade of the red powder

Fig. 14 Effect of 1-pentanol/chloroform ratio on the red fluorescent powder separation to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: solid/liquid 30 g/L, 0.25% PST in aqueous phase, pH 7 of aqueous phase)

Fig. 15 Effect of solid concentration on separation results of the red fluorescent powder to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: organic/aqueous ratio 2/3, 0.25% PST in aqueous phase, pH 7 of aqueous phase, 1-pentanol/chloroform ratio 1/4)

to the aqueous phase.

1-Pentanol is needed to improve the efficiency of the separation (Fig. 14). Usually 1-pentanol is used as a frother¹²⁾. The suitable ratio of 1-pentanol/chloroform (by volume) is from 0.2 to 0.5. In this range, the grade and recovery of red product exceed 90% as 1-pentanol enhances the extractive ability of chloroform. 1-Pentanol was acted as a stabilizer, which stabilized the chloroform drop-

Fig. 16 Effect of number of extractions on the extraction of the red powder to the aqueous phase at first extraction step of the flow sheet 2. (Experimental conditions: organic/aqueous ratio 2/3, 0.25% PST in aqueous phase, pH 7 of aqueous phase, 1-pentanol/chloroform ratio 1/4)

lets dissolved inside the aqueous phase because hydroxyl ion of 1-pentanol was attractive to the water molecule while hydrocarbon radical of 1-pentanol was reactive to the chloroform molecule. At higher concentration of 1-pentanol, grade and recovery of the red powder decreased to 70.8% and 62.5%, respectively. This trend may be attributed by crowding effect caused by excess 1-pentanol particles in the solution effectively colliding chloroform particle from accessing the green and blue powders. The stability of chloroform droplet was increased with increasing the amount of 1-pentanol added.

Furthermore, the effect of solid concentration in the extraction is considered. The change of the grade and distribution of red powder at different solid/liquid ratio is shown in Fig. 15. The better ratio of solid/liquid is from 5 to 30 g/L, because the fine powders interfere with each other in the extraction system such as agglomeration, adhesion and impulsion. It is not suitable to conduct the separation when the solid concentration is lower or higher than appropriate concentration. Low solid concentration gives suspended red particles less opportunity to collide each other that leads to aggregation of the particles. Lower recovery and high grade are obtained at low solid concentration. On the other hand, high solid concentration gives suspended red particles more opportunity to collide each other that leads to aggregation of the particles. High recovery and lower grade are obtained at high solid concentration because of involution

of other blue and green powders. Brownian coagulation is occurred when Brownian particles are collided each other in liquid.

Separation of the red powder from artificial mixture can be improved by increasing the number of extraction. The repeated process is carried out in the same extraction condition and the result is shown in Fig. 16. The lower numbers of extractions were conducted, the more solid concentration of fluorescent powders was treated during the extraction. High solid concentration gives suspended red particles more opportunity to collide each other that leads to aggregation of the particles. High recovery and low grade were obtained at high solid concentration because of involution of other blue and green powders. Therefore, one time extraction gave high recovery (94.2%) and low grade (73.5%). On the other hand, the more numbers of extractions were conducted, the lower solid concentration of fluorescent powders was treated during the extraction. Low solid concentration gives suspended red particles less opportunity to collide each other that leads to aggregation of the particles. Less recovery and high grade are obtained at low solid concentration. Therefore, three times extraction lower recovery (89.2%) and higher grade (93.6%). With decreasing the recovery of the red powder, the grade increases. This is general relationship between recovery and grade¹³⁾. Three or four times of extraction are necessary to separate the red fluorescent powder from the others powders with good recovery and grade at efficiency of higher than 80%. In this case, the separation has been conducted through three times of extraction.

3.3 Separation of blue fluorescent powder from green fluorescent powder following flow sheet 2 (Second extraction step)

pH values of the aqueous phase and HTTA concentration on the second step of flow sheet 2 were observed. The relationship between the extraction results and pH value is shown in Figs. 17 and 18. Obviously, the optimum pH value is 10.3 at efficiency of 59.3% of the blue powder and 57.2% of green powder. Concentration of HTTA species as a function of pH values of aqueous phase was studied in Fig. 5. Lower than pH 10, the amount of reactive HTTA species, TTA^- was mostly smaller than the amount of non-reactive HTTA species, HTTA. The blue powder containing Ba^{2+} ion was not strongly attracted by TTA^- due to the low concentration of TTA^- and were not obtained flotability. At pH 10, TTA^- was abundant in the solution. TTA^- was reactive to Ba^{2+} ion of the blue powder, which was obtained flotability. Higher than pH 11,

Fig. 17 Effect of pH value on separation of the blue powder to the aqueous phase at second extraction step of the flow sheet 2. (Experimental conditions: 1% HTTA in heptane phase, solid/liquid ratio 30 g/L, 1% PST in aqueous phase, organic/aqueous ratio 2/3)

Fig. 18 Effect of pH value on extraction of the green powder to the heptane phase at second extraction step of the flow sheet 2. (Experimental conditions: 1% HTTA in heptane phase, solid/liquid ratio 30 g/L, 1% PST in aqueous phase, organic/aqueous ratio 2/3)

hydroxyl ion was abundant in the aqueous solution, which competed with TTA^- to react with Ba^{2+} ion. The competitive adsorption limited the flotability of the blue powder to the heptane phase, which decreased the extraction rate of the blue powder at higher than pH 10.

Effect of HTTA concentration on the extraction results of the blue and green powders was observed (Figs. 19 and 20). With decreasing HTTA

Fig. 19 Effect of HTTA concentration on separation of the blue powder to the aqueous phase at second extraction step of the flow sheet 2. (Experimental conditions: pH 10.3 of the aqueous phase, solid/liquid ratio 30 g/L, 1% PST in aqueous phase, organic/aqueous ratio 2/3)

Fig. 20 Effect of HTTA concentration on separation of the green powder to the heptane phase at second extraction step of the flow sheet 2. (Experimental conditions: pH 10.3 of the aqueous phase, solid/liquid ratio 30 g/L, 1% PST in aqueous phase, organic/aqueous ratio 2/3)

concentration, the efficiency of the separation of the blue powder was improved significantly. The best results are obtained when HTTA concentration is at 2.5 g/L at efficiency of 80.8% of the blue powder and 81.2% of the green powder. However, when HTTA concentration was higher or lower than 2.5 g/L, the blue powder cannot be well extracted and its recovery and grade was decreased. Low concentration of HTTA gives less flotability

Fig. 21 Electric conductivity of aqueous solution at pH 10 as a function of HTTA concentration.

to the blue powder and high concentration of HTTA gives more flotability to the green powder contaminating the blue powder recovering in the heptane phase. Measurement of electric conductivity of aqueous solution at pH 7 as a function of HTTA concentration was conducted to observe the critical micelle concentration of PST (Fig. 21). Bending point of the graph was observed at HTTA concentration of 0.015%. Lower than HTTA concentration of 0.015%, free reactive HTTA species, TTA^- , which reacted with the blue powder, was abundant. Higher than HTTA concentration of 0.015%, TTA^- started micelle formation and the concentration of these HTTA species were gradually decreasing. Therefore, effect of HTTA on attaching the blue powder at HTTA concentration of below 0.015% was lower than the effect at HTTA concentration of higher than 0.015%. Less effect of HTTA on attaching the blue powder decreased the grade of the red powder to the aqueous phase. However, concentration of HTTA was 0.15–1.0% during the extraction, which was larger than the critical micelle concentration of HTTA measured. Therefore, the trend of the extraction of the blue and green powders was due to the high concentration of HTTA. High concentration of HTTA increased the involution of the green powder to the heptane phase and decreased the grade and recovery of the blue powder to the heptane phase.

3.4 Comparison of two flow sheets for separating three kinds of fluorescent powders

Two different flow sheets are proposed for the separation of red (Y_2O_3 : Eu^{3+}), blue ($\text{BaMgAl}_{10}\text{O}_{17}$: Eu^{2+}) and green ($\text{CeMgAl}_{10}\text{O}_{17}$: Tb^{3+}) fine fluorescent powders as described in the previous sections (Sections 3.1–3.3). To compare the two flow sheets, efficiency of liquid-liquid extraction was calculated by using Eq. (2). Data used

Table 2 Separation results and efficiency of the separation of the fluorescent powders following the flow sheet 1.

Red		Green		Blue		Efficiency (%)
Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	
96.9	94.1	94.6	76.0	74.1	98.7	47.9

Table 3 Separation results and efficiency of the separation of the fluorescent powders following the flow sheet 2.

Red		Green		Blue		Efficiency (%)
Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	
86.9	92.7	83.0	64.1	60.2	78.5	20.3

for the calculation of efficiency were separation results of the fluorescent powders by following the flow sheets 1 and 2 at optimized experimental conditions (Tables 2 and 3). Efficiency of the separation of the fluorescent powders following the flow sheet 1 (47.9%) was higher than efficiency of the separation following the flow sheet 2 (20.3%) (Tables 2 and 3). Differences between flow sheet 1 and 2 were the order of the extraction step and the existence of washing treatment by ethanol. Following the flow sheet 2, the first separation of red fluorescent powder effected badly on the separation of the blue and green powders because the surface of the blue and green powders has been contaminated with particles of other fluorescent powders and a surfactant, which cannot be remedied well by washing and drying treatment.

4. Conclusions

- (1) Liquid-liquid extraction using aqueous and organic phases was an effective method to separate red (Y_2O_3 : Eu^{3+}), blue ($\text{BaMgAl}_{10}\text{O}_{17}$: Eu^{2+}) and green ($\text{CeMgAl}_{10}\text{O}_{17}$: Tb^{3+}) fine fluorescent powders.
- (2) Two different flow sheets were proposed for the separation of the fluorescent powders. In flow sheet 1, the blue powder was first extracted into the upper phase (heptane), using a chelating agent HTTA at the pH range from 7 to 11. The green and red powders remained in the lower phase (aqueous). The green powder was then extracted into chloroform phase and separated from the red powder, which remained in the aqueous phase, with a depressant, PST. In flow sheet 2, the red powder was extracted into the upper phase (aqueous). The green and blue powders remained in the lower phase (chloroform), using PST at the pH range from 7 to 11. The blue powder was then extracted into heptane phase and separated from the green powder, which remained in the aque-

ous phase with PST.

- (3) To compare the two flow sheets, efficiency of liquid-liquid extraction has been calculated. Flow sheet 1 for liquid-liquid extraction of the fluorescent powders using heptane-aqueous phases obtained higher efficiency than flow sheet 2 for liquid-liquid extraction of the fluorescent powders using chloroform-aqueous phases.
- (4) The grade and recovery of separated products by following the flow sheet 1 at optimized experimental conditions were as follows; red powder: 96.9% and 94.1%; blue powder: 74.1% and 98.7%; green powder: 94.6% and 76.0%, respectively.

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