

# PRODUCTION OF MALACHITE GREEN BY OXIDATION OF ITS LEUCO BASE USING POTASSIUM PERSULPHATE, POTASSIUM PERMANGANATE AND MANGANESE DIOXIDE

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## ABSTRACT

Malachite green dye was produced by oxidising the Malachite leuco base with some inorganic oxidants. Best product yield was obtained with manganese dioxide, while potassium permanganate gave better results than potassium persulphate. Dye yield was influenced by the optimum quantity of oxidant applied

**KEY WORDS:** Leuco Base, Oxidant, Dye, Yield.

## INTRODUCTION

Malachite green belongs to the Basic Triphenylmethane dyes which are produced by condensation reactions involving aldehydes and aromatic amines (Fischer, 1883). In the presence of zinc chloride or oxalate salts, the initial condensation product is a triphenyl derivative called leuco base. The leuco base is then oxidized to malachite green. Attempts have been made to synthesize the dye without passing through the leuco base (Sen and Mukherji, 1929), but generally a leuco malachite green is produced, followed by oxidation of the base (Fischer, 1883; Yoshino, 1942). The amount of dye produced depends on the leuco base oxidation process. Using lead dioxide as an oxidant, the freshly prepared sample is preferred as commercial grade lead dioxide does not react very well (Fischer, 1883).

Malachite green is used for the solvent extraction of ions such as antimony (Sato et al 1983) and tungsten (Patil, and Turel, 1995). It is also used for the spectroscopic determination of trace concentrations of phosphate (Carter and Karl, 1983) and arsenic (Quan-Feng and Peng-Fei, 1983). As a triphenylmethane dye, malachite green is used as a direct dye for silk, wool, jute and leather. When mordanted with tannin, it can be used to dye cotton (Finar, 1980). It has also been used to determine trace amounts of chromium (III) in leather (Balasubramanian and Padmaja, 1997). Malachite green finds application as a local antiseptic and is effective against fungi and gram-positive bacteria. It has been used as an anti-microbial agent for controlling decay of seed potatoes (Shashirekha and Narasimham, 1987). The dye is used in

printing inks (Mayer and Kast, 1974) and has been reported to provide stable colour tone, in conjunction with other dyes, for printed circuit boards (Kushi et al 1994). Malachite green is imported into Nigeria and is commercially used in insect repellants such as mosquito coils and in the manufacture of terrazzo floor tiles among other uses.

In an attempt to produce this dye locally and for cost effectiveness, the suitability of some inorganic oxidants in the leuco base oxidation process was investigated and the results reported in this paper.

## MATERIAL AND METHODS

### Material

Manganese dioxide, potassium permanganate, zinc chloride, benzaldehyde and hydrochloric acid were obtained from BDH. Potassium persulphate, Dimethylaniline and ethanol were supplied by Aldrich Chem. Co. Sodium hydroxide was of M&B while sodium chloride was obtained locally as common salt. To ascertain purity, the melting points of leuco base and malachite green were determined with Galemkamp Melting point Apparatus (Registered Design No 889339 and Cat. No 17/MF 370). Initial weights were determined using Mettler H 160 analytical balance (Max. 160g, d = 0.1mg) and rounded up to two decimal points. Later measurements were carried out on Mettler PC 2000, top loading balance, Spectrophotometric measurements were carried out on Unicam double beam UV-Visible scanner.

## Experimental

The leuco base was prepared by Fisher's method (Fischer, 1883). Zinc chloride, dimethylaniline and benzaldehyde were mixed in a reaction flask and heated for 4h. Excess dimethylaniline was removed by steam distillation. The residue was dissolved in ethanol, warmed and cooled. The crystals formed, were collected by filtration and the melting point was determined to be 98 – 100°C.

### Oxidation of Leuco Base:

Leuco base (5.5g) was dissolved in dilute HCl (400cm<sup>3</sup>) in a beaker. 400cm<sup>3</sup> of H<sub>2</sub>O was added and the solution was cooled in an ice bath. With continuous stirring, the oxidant, mixed with 30cm<sup>3</sup> of H<sub>2</sub>O, was added in small portions over a period of 15min. The mixture was stirred for another 20min. and filtered. ZnCl<sub>2</sub> (6.0g), dissolved in 10cm<sup>3</sup> of H<sub>2</sub>O, was added to the filtrate and the solution was continuously stirred for another 20 min. NaCl (40.0g) was added to the solution and the mixture was removed from the ice bath and allowed to stand overnight. It was filtered and washed with salt water (5.0g of NaCl in 40cm<sup>3</sup> of H<sub>2</sub>O). The crude product was dried in air for 24h and weighed. It was then dissolved in 150cm<sup>3</sup> of hot H<sub>2</sub>O, filtered on a fluted filter paper and allowed to cool. NaCl (15.0g) was added to the solution and the pure product, which was salted out, was filtered, washed with salt water and air-dried. Melting point was determined to be 127-128°C.

## RESULTS AND DISCUSSION

At an initial oxidant concentration of 0.01M, (Table 1), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> gave 0.19g of recrystallised dye product. As the quantity of oxidant was doubled, dye yield decreased to

0.12g. Increasing the oxidant concentration to 0.03M produced a drop in dye yield to 0.08g which is three-quarters of the yield obtained at 0.02M of oxidant. At 0.04M of oxidant, a dye product yield of 0.03g was obtained. This yield is about one-half and one-quarter of the yields obtained at 0.03M. and 0.02M of oxidant concentrations respectively. Thus, the dye product yield decreased six folds as the concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was increased from 0.01 to 0.04M. At 0.05M of oxidant, no dye was produced. These results show that the quantity of oxidant used has influence on the dye product yield (Fischer, 1883). The optimum oxidant concentration was 0.01M of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The leuco base and the malachite green dye produced are shown in the chemical equation in scheme 1.

In Table II, the use of 0.01M of KMnO<sub>4</sub> oxidant, gave 0.62g of recrystallised dye product.

Twice the amount of oxidant slightly increased the yield to 0.65g. increasing the amount of oxidant to 0.03M led to an increase in product yield to 0.74g. At 0.04m of oxidant, dye yield reduced considerably to 0.06g. Further increase in oxidant concentration gave a product yield of 0.03g which is one-half of that obtained at 0.04M of oxidant. The optimum oxidant concentration as also 0.01M of KMnO<sub>4</sub> based on % yield.

The use of 0.01M of MnO<sub>2</sub> oxidant, Table III, gave a recrystallised product yield of 2.06g. Twice the amount of oxidant increased the product yield to 3.23g. At 0.03M of oxidant, the dye yield increased slightly to 3.26g which is about five times and ten times the yields obtained at 0.04M and 0.05M of Oxidant respectively.

These results are explained from the fact that the amount of dye produced depends on the quantity of oxidant used in the leuco base oxidation process. As the quantity of oxidant

Table 1: Dye Product Yield by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidant

Amount of oxidant used (M)	Yield (g)		% Yield (Recrystallized)
	Crude	Recrystallized	
0.01	5.71	0.19	3.33
0.02	9.32	0.12	1.29
0.03	15.76	0.08	0.51
0.04	18.80	0.03	0.16
0.05	21.63	0.00	0.00

Table 2 :Dye Product Yield by KMnO<sub>4</sub> oxidant

Amount of oxidant used (M)	Yield (g)		% Yield (Recrystallized)
	Crude	Recrystallized	
0.01	3.45	0.62	17.97
0.02	4.64	0.65	14.01
0.03	6.92	0.74	10.69
0.04	9.87	0.06	0.61
0.05	13.79	0.03	0.22

Table 3 : Dye Product yield by  $MnO_2$  oxidant

Amount of oxidant used (M)	Yield (g)		% Yield (Recrystallized)
	Crude	Recrystallized	
0.01	4.13	2.06	49.88
0.02	5.50	3.23	58.73
0.03	6.26	3.26	52.08
0.04	10.70	0.67	6.26
0.05	14.22	0.32	2.25

increases to an optimum concentration, a maximum dye product yield is obtained. Increasing the quantity of oxidant beyond its optimum concentration introduces excess oxidant in the system. The excess oxidant now acts on the dye already produced and converts it to a quinone imine (Kehramann et al, 1922). Further oxidation may lead to the cleavage of methyl groups from the malachite green.

Comparing Tables I and II, an optimum product yield of 0.19g was obtained at 0.01M of  $K_2S_2O_8$  oxidant while that of  $KMnO_4$  was 0.74g obtained at 0.03M of oxidant. The optimum product yield obtained with  $KMnO_4$  is four times greater than that of  $K_2S_2O_8$ . Besides, higher yields were obtained with  $KMnO_4$  at all concentrations. These results show that  $KMnO_4$  is better than  $K_2S_2O_8$  in the leuco base oxidation process. There was little or no dye yield from both oxidants at a concentration of 0.05M because this amount of oxidant was such that whatever dye yield obtained was completely or almost completely oxidized to other products.

When Tables II and III are compared, an optimum dye product of 3.26g was also obtained at 0.03M of  $MnO_2$ . This yield is four and half times greater than the yield obtained with  $KMnO_4$ . In addition, higher product yields were obtained with  $MnO_2$  at all concentrations. Thus,  $MnO_2$  is better than  $KMnO_4$  in the oxidation of Malachite leuco base. Furthermore, the dye yield obtained at 0.05M of  $MnO_2$  is greater than the optimum yield obtained at 0.01M of  $K_2S_2O_8$  in Table I. Thus  $MnO_2$  is much more suitable than  $K_2S_2O_8$  in leuco base oxidation. The crude yield from  $K_2S_2O_8$  was higher, at each oxidant concentration, than the crude yields from  $KMnO_4$  and  $MnO_2$  respectively. High crude yields, according to Agunwa and Okonkwo (2000), may be due to impurities in the oxidant.

The variation of % yield of dye product with oxidant concentration is shown in Figure 1. The % yields of  $K_2S_2O_8$  and  $KMnO_4$  oxidants decreased as oxidant concentration increased, while that of  $MnO_2$  increased slightly and then decreased as oxidant concentration increased.

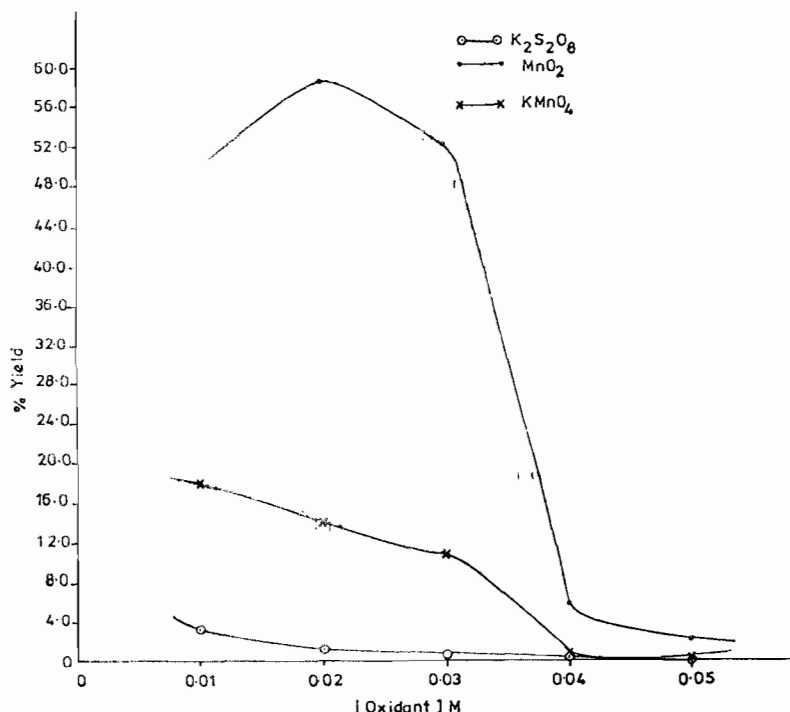


FIG. 1: VARIATION OF PERCENTAGE YIELD OF DYE WITH OXIDANT CONCENTRATION

The % yields of both  $MnO_2$  and  $KMnO_4$  are higher than that of  $K_2S_2O_8$  at all concentrations. The graph clearly shows the suitability of  $MnO_2$  over  $KMnO_4$  and  $K_2S_2O_8$  in the leuco base oxidation process. In glacial acetic acid, the absorption spectra of the malachite green samples produced had highest extinction coefficient,  $\epsilon = 10.1 \times 10^{-4}$ , at  $\lambda_{max}$  620 nm.

## CONCLUSION

In the production of malachite green by oxidation of malachite leuco base with  $MnO_2$ ,  $KMnO_4$  and  $K_2SO_8$ , best product yield was obtained in the order  $MnO_2 > KMnO_4 > K_2S_2O_8$ . Dye yield was affected by the concentration of oxidant used. A minimum oxidant concentration for best yield of dye was 0.01M for both  $K_2S_2O_8$  and  $KMnO_4$ , and 0.02M for  $MnO_2$ .

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