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STUDY ON LUMINOUS PROPERTIES AND FORMULATIONS OF SOME ILLUMINATING COMPOSITIONS BASED ON UPE AS POLYMERIC BINDERS

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ABSTRACT

Illuminating compositions based on unsaturated polyester binders have been prepared. This work was directed towards the application of unsaturated polyesters as an oxygen containing binder for an illuminant composition. In this work, the effect of variation of the different formulating parameters on the processing and luminous characteristics of the illuminant composition has been investigated.

Those parameters include; changing type and content of metallic fuel such as magnesium and aluminum, inorganic oxidizer such as sodium, barium and strontium nitrate as well as the polymeric binder. The binder used was rigid and flexible unsaturated polyester. The effect of addition of sodium fluoride, poly vinyl chloride, and graphite to the illuminant composition has been also studied.

This work shows that unsaturated polyester can be fairly used as a typical polymeric binder for preparing an illuminant composition of high luminous and mechanical characteristics.

INTRODUCTION

Testing of many prior art flare compositions based on various binder formulations shows that high oxygen content in the binder improves efficiency. Cold polymerizing plastics such as unsaturated polyesters (Laminac) are typical examples of such oxygen rich binders^[1].

The intensity of an illuminating composition is largely determined by its temperature, which in turn depends on the stability of the reaction products. In order to generate grey body radiation which encompasses the spectral sensitivity of the human eye (0.4 - 0.74 μm), 3000 °K should be exceeded. Whereas this is possible using nitrates and perchlorates^[2] with alkaline earth metals as well as Zr, Ti and Hf, in practice Mg and Al are found to be best in terms of heat output, cost, and transparency to visible radiation.

The chemical ingredients in pyrochemical compositions can be divided into: fuels, oxidizers, binders (adhesives), and accessory materials. Metal oxidizers contribute their energy in the form of spectral emission at characteristic frequencies. The Common oxidizers include Sr (NO₃)₂, NaNO₃, and Ba (NO₃)₂^[3].

Most of the binders are natural and synthetic polymers. Among the synthetic polymers are silicon rubbers, epoxy resins, polyurethanes, carboxyl terminated polyesters cured by epoxy compounds, homopolymers and copolymers of vinyl monomers^[4] as alkylene oxides, acrylonitrile, and dienes.

Some compounds are added to the illuminant composition to increase the intensity of light. These compounds are known as flame forming agents. A typical example of these compounds is sodium fluoride^[5].

Strong hydraulic consolidation pressures, mostly, in the range of 6000 to 30,000 psi, are exerted on illuminating powder compositions within a steel or brass mold.

The burning time of the flare candle varies with the particle size and shape of the major ingredients.

This work is directed towards the study of the effect of different formulating parameters on the processing and luminous characteristics of the illuminant composition.

EXPERIMENTAL

Formulation Of Illuminant Composition

Illuminant compositions based on unsaturated polyesters have been prepared in the laboratory. The method of preparation includes the steps of mixing the prepolymer binder components, adding the metallic fuel followed by the oxidizer and other additives. After completion of mixing process the illuminant mixture is pressed while still wet inside a steel container. Then allowed to cure (for 16-24 hours) after pressing at room temperature to form an illuminant candle. Hydraulic consolidation pressure of about 14000 psi has been exerted.

In case of granulation process an evaporable diluent (acetone) has been added to the prepolymer binder and after completion of the mixing process the pyrotechnic composition incorporating the diluent mixture has been forced to pass through a sieve with 2mm mesh to form granules. The curing and evaporation processes are then allowed to complete. This may be allowed to take place while the composition is still in granular form; the granules can then be pressed into a solid mass. Alternatively, the granules can be pressed together while the curing and evaporation processes are taking place which enables a lower pressure to be employed. In either case a mechanically strong mass having cured unsaturated polyester as the

binder has been prepared. Materials used for the polymeric binder in the studied formulations and their characteristics are listed in table 1.

The preparation technique may be conducted either with the binder alone or with the binder-diluent mixture. The used binders were rigid and flexible unsaturated polyester. Methyl ethyl ketone peroxide as the polymerization catalyst was added to the styrenated polyester and mixed well. Then cobalt octoate as an accelerator to promote the curing process at room temperature was added to the previous mixture. The used oxidizers were sodium nitrate, barium nitrate and strontium nitrate, while Al and Mg powders were used as metallic fuels.

Various formulations using different types and contents of binder, oxidizer and metallic fuel have been prepared. Also different grain sizes of the oxidizers and fuels have been used. Sodium fluoride was used as an active flame forming agent. Tables 2, 4, 6 illustrates the detailed formulation for the prepared illuminant compositions.

The detailed method for preparation of the suitable binder composition is explained in preceding article^[6]. The illuminant compositions were consolidated into a steel cylindrical containers (with 84 mm inner diameter) and cured at room temperature. The oxidizers and metallic fuels were used in bimodal composition 30% <50 μm ; 70% between 50 and 150 μm for fine powder, and 30% < 100 μm ; 70% between 100 and 250 μm for coarse powders. Sodium fluoride was used in grain size < 50 μm , while graphite <100 μm and PVC is of the emulsion type.

Luminous and Explosive Characteristics:

Measurement of candle power output and burning time was carried out using the channel light beam oscillograph type H 115. The ignition temperature and calorific value were determined by following the procedures outlined in analytical methods for powders and explosives.^[7-8]

RESULTS AND DISCUSSION

To show the effect of variation of binder content on luminous characteristics, five illuminant formulations were prepared (Nos. 1-5 in Table 2). The luminous characteristics tabulated in table 3 and illustrated in Fig.(1) show that increasing the binder (UPE) content from 4% to 13.5% causes a pronounced decrease in candlepower output and burning rate. Also the efficiency increases up to a maximum value at binder content 9.3% by weight then it starts to decrease again. It is clear too, that the inflection point of the candle power output curve and the peak of the luminous efficiency curve corresponds, to the inversion of $\text{Ba}(\text{NO}_3)_2$ to $\text{Sr}(\text{NO}_3)_2$ mass ratio from 1:5 to 5:1 respectively. From table 2 it is clear that the decrease of the content of NaF (as the flame forming agent) from 3.8% to 1% causes a decrease in c.p.o. and luminous efficiency but a very slight change in b.r. Luminous efficiency is defined by multiplying the candle power into time of burning and then divided by the mass of the illuminant composition ($\text{cd} \cdot \text{sec}/\text{gm}$).

To make a correlation between luminous characteristics and the binder content in illuminant compositions containing $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ in addition to NaNO_3 (as the major portion of the oxidizer mixture), six samples (Nos. 7-12 in table 4) were prepared in variable content of UPE from 9% up to 16.1%. Table 5 and Fig. (2) show that the increase of binder content causes a decrease in c.p.o. and b.r. However, the efficiency increases slowly with the increase of binder up to 14.5% then decreases again. The inflection point of the c.p.o. curve and the peak point of luminous efficiency curve corresponds to the use of pure UPE as liner between the illuminant composition and the inner walls of the steel container. The use of UPE liner as thermal insulation minimizes the energy loss from the burning candle and also prolongs the time of burning because it decreases the heating up of the remaining composition with hot combustion products by conduction through the container walls. At higher values of binder content $>14.5\%$ the c.p.o. decreases dramatically due to

chemistry formation and shortening of b.r. The addition of PVC by 1.8% to the illuminant composition causes a remarkable decrease in c.p.o. and luminous efficiency but no change nearly in b.r., this may be attributed to the low temperature of dissociation of PVC and the endothermic nature of this reaction.

Another study was carried out aimed at illustrating the effect of using NaNO_3 as the only oxidizer, the effect of grain size of NaNO_3 and Mg, the addition of graphite and finally the effect of variation of the oxd. / ful. ratio^[9]. The composition of the illuminant formulations shown in table 6.

The dependence of luminous characteristics on the different mentioned parameters is shown in table 7. It is clear from table 7 that the use of NaNO_3 as oxidizer improves significantly the c.p.o. and luminous efficiency, also as the grain size of NaNO_3 increases (up to 210 μm) the c.p.o. and luminous efficiency increase.

The same effect of grain size variation is shown for Mg which may be explained by the rapid decrease in burning time as the grain size decreases leading to decrease in luminous efficiency. The addition of 1 % graphite causes an increase in c.p.o. and dramatic decrease in burning time, thus leading to a decrease in luminous efficiency.

The dependence of luminous characteristics on the oxidizer to fuel ratio is illustrated in Fig. (3) and Fig. (4). It is clear that, luminous efficiency increases with the increase of oxd./ful. from 0.43 to 0.52 then starts to decrease slightly again from 0.52 to 0.58. However, the c.p.o shows slight increase and b.r. shows rapid increase in their values with the increase of oxd/ful Ratio to the value .58. This may be explained by the optimum stoichiometry of the reactants at the value .52 followed by rapid decrease in burning time at .58 due to excess oxidizer leading to decrease in luminous efficiency.

The use of flexible UPE improves significantly all the luminous characteristics as shown in table 7. This may attributed to the lower content of styrene in flexible UPE compared to rigid UPE which means the minimizing of the bad effect of styrene on the luminous characteristics.

CONCLUSION

Illuminating compositions of attractive luminous characteristics could be obtained using unsaturated polyesters as an oxygen rich polymeric binders. The grain size of both oxidizer and fuel affects greatly the luminous characteristics of the prepared compositions. Sodium nitrate as oxidizer gives better results than $\text{Ba}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$.

NOMENCLATURE

UPE : unsaturated polyester

PVC : Poly vinyl chloride

cd : candle

b.r. : burning rate

r.m.f : rate of mass flow

c.p.o : candlepower output

oxd : oxidizer

ful : fuel

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Table 1 . Sources and Specifications of Materials of Polymeric Binders

Materials	Specifications	Source
Rigid unsaturated polyester	Medium reactive isophthalic polyester solution of 33% by wt. Styrene content	Egyptian American Company for Paints &Coatings
Flexible unsaturated polyester	Resilient isopolyester solution of 28% by wt. Styrene monomer content	
Methyl ethyl ketone peroxide	Colourless liquied, irritant used as polymerization catalyst	
Cobalt octoate	As solution containing 10% by wt. of cobalt octoate in styrene	

Table 2. Formulation of illuminant compositions containing barium and strontium nitrate.

Composition mass %	Constituents					
	UPE	Al	Mg	NaF	Ba(NO ₃) ₂	Sr(NO ₃) ₂
S1	4	5	57	4	5	25
S2	6.8	4.9	55.3	3.8	4.9	24.3
S3	9.3	4.7	53.9	3.8	4.7	23.6
S4	11.1	4.6	52.8	3.7	23.2	4.6
S5	13.5	4.5	51.4	3.6	22.5	4
S6	9.1	5.7	56.5	1	23.9	4.8

Table 3 . Luminous characteristics of illuminant compositions containing barium and strontium nitrate

Formulations No.s	Burning Rate (cm/s)	Mass Flow Rate (g/s)	Candle Power Output (cd)	Luminous Efficiency (cd.s/g)
S1	1.25	98	1,910,000	13,500
S2	0.59	44.8	1,360,000	30,400
S3	0.47	36	1,115,000	31,000
S4	0.57	43.6	992,000	22,800
S5	0.45	33.9	522,000	15,400
S6	0.60	45.5	797,000	17,500

Table 4. Formulation of illuminant compositions containing barium, strontium and sodium nitrate.

Composition mass %	Constituents					
	UPE	Mg+AL	NaNO ₃	Ba(NO ₃) ₂	Sr(NO ₃) ₂	PVC
S7	9	62.0	22.0	5.0	4.0	-
S8	13.1	60.0	19.1	4.3	3.5	-
S9	14.5	59.0	18.8	4.3	3.4	-
* S10	14.6	59.2	18.7	4.7	3.8	-
* S11	15	57.9	18.7	4.7	3.7	-
* S12	16.1	57.1	18.4	4.6	3.7	-
S13	14	57.5	18.6	4.6	3.7	1.8

Table 5. Luminous characteristics of illuminant compositions containing barium, strontium and sodium nitrate

Formulations No.s	Burning Rate (cm/s)	Mass Flow Rate (g/s)	Candle Power Output (cd)	Luminous Efficiency (cd.s/g)
S7	0.51	42.9	1,539,000	36,100
S8	0.38	31.8	1,130,000	37,100
S9	0.34	28.4	1,018,000	35,900
* S10	0.26	20.8	825,000	39,600
* S 11	0.25	20	538,000	37,000
* S 12	0.24	19	704,000	21,400
S13	0.35	27.8	758,000	27,00

Table 6. Formulation of illuminant compositions containing sodium nitrate only

Composition mass %	Constituents						
	NaNO ₃		Mg		Graphite	Other Additives	oxd Ful.
	Fine	Course	Fine	Course			
S14	30.4	-	-	48.4	-	21.2	0.58
S15	30.4	-	24.2	24.2	-	21.2	0.58
S16	27.9	-	-	50.1	-	22.0	0.52
S17	24.4	-	-	52.8	1	21.8	0.43
S18	24.6	-	-	53.4	-	22.0	0.43
S19	-	27.9	-	50.1	-	22.0	0.52
**S20	-	28.7	-	49.2	-	21.8	0.54

Table 7. Luminous characteristics of illuminant compositions containing sodium nitrate only

Formulations No.s	Burning Rate (cm/s)	Mass Flow Rate (g/s)	Candle Power Output (cd)	Luminous Efficiency (cd.s/g)
S14	0.23	18.2	1,070,000	58,000
S15	0.29	23.3	1,031,000	41,000
S16	0.18	14.3	917,000	63,000
S17	0.32	26.9	1,375,000	51,000
S18	0.16	13.2	780,000	59,300
S19	0.21	16.9	1,136,000	67,000
** S20	0.23	17.9	1,397,000	77,900

Note: - In tables 4 and 5 the symbole (*) means with the use of UPE as thermal insulation.
 - In Tables 6 and 7 the symbole (**) means that the binder used is flexible unsaturated polyester, other additives means the sum of Al, NaF and UPE.

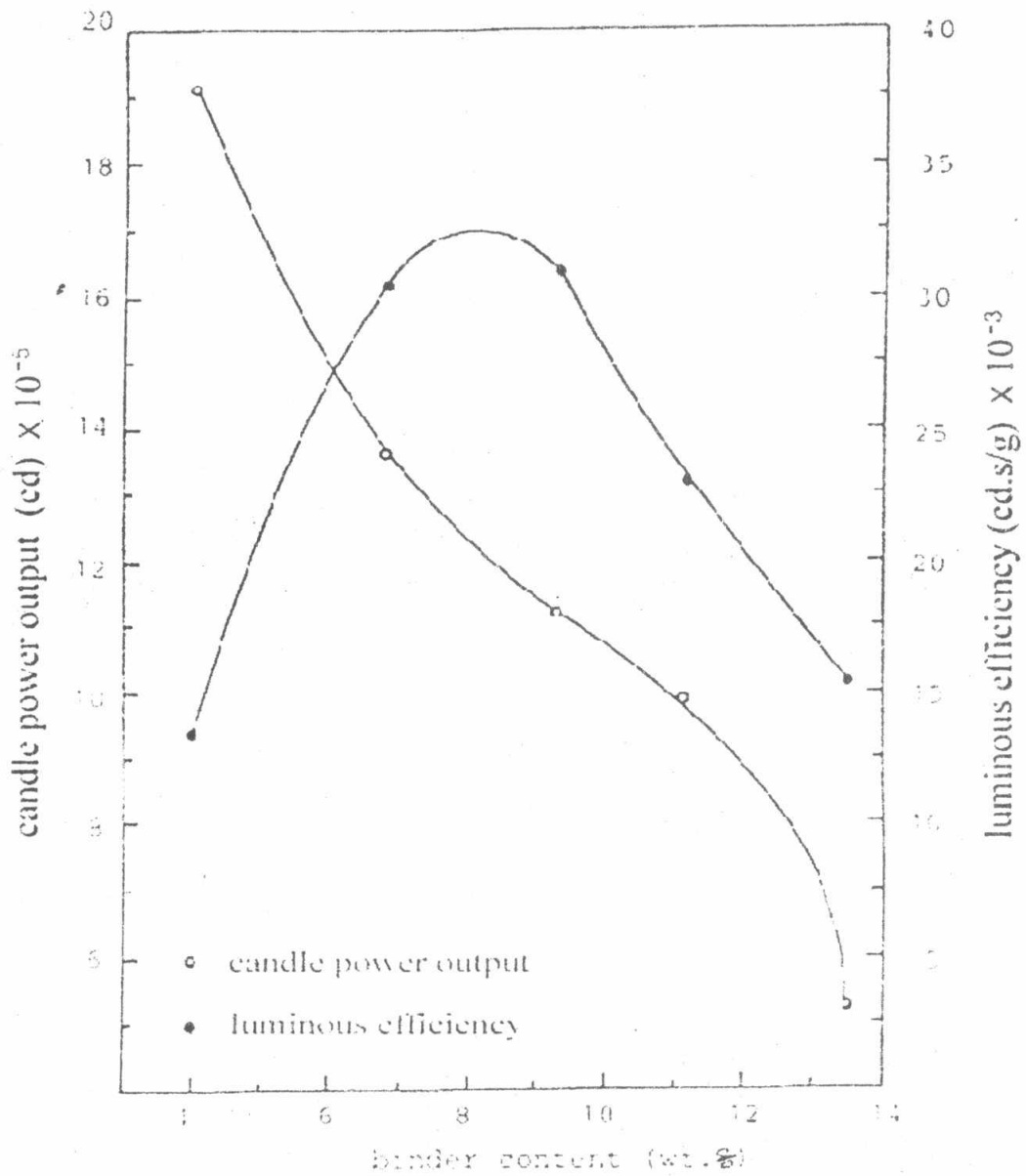


Fig. (1): Effect of binder content on candle power output and luminous efficiency for compositions containing barium and strontium nitrate.

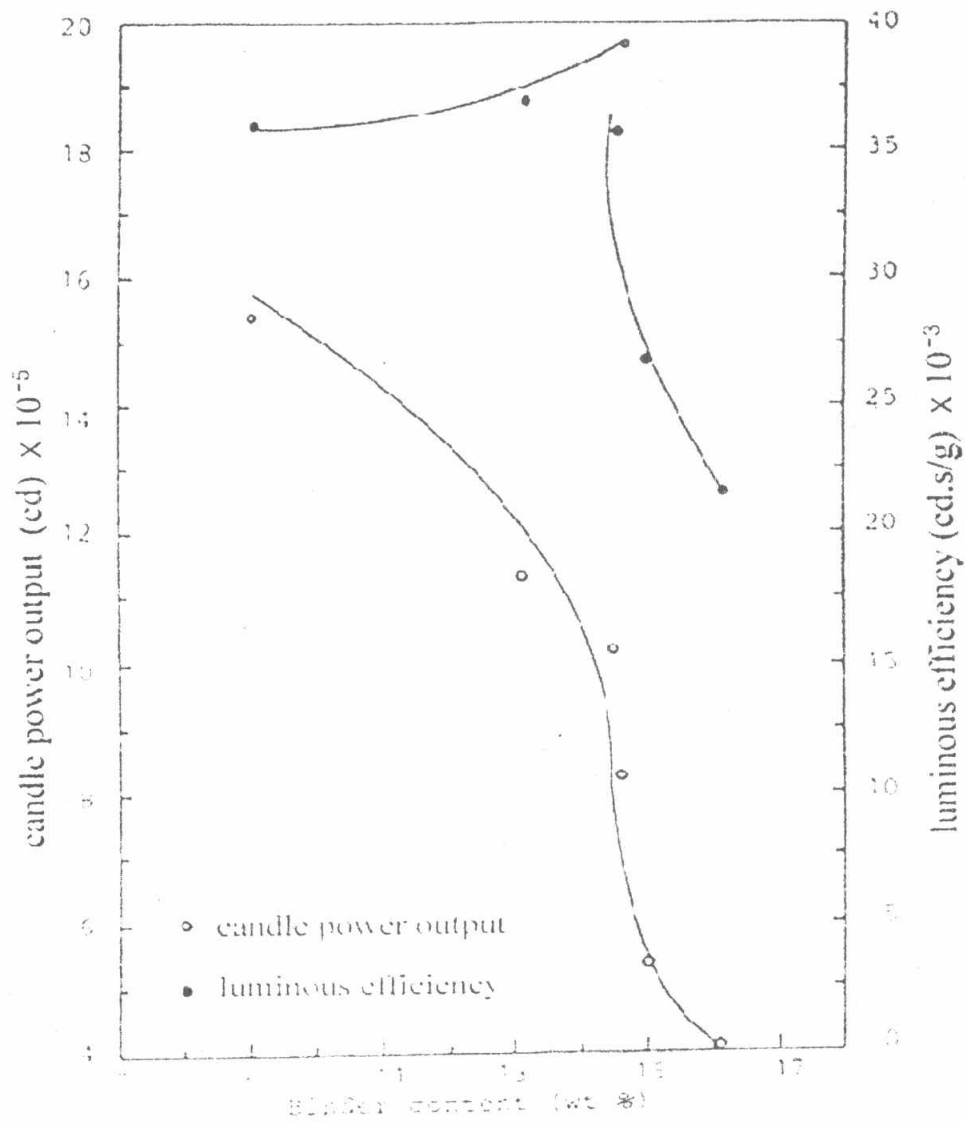


Fig. (2): Effect of binder content on candle power output and luminous efficiency for compositions containing barium, strontium and sodium nitrate.

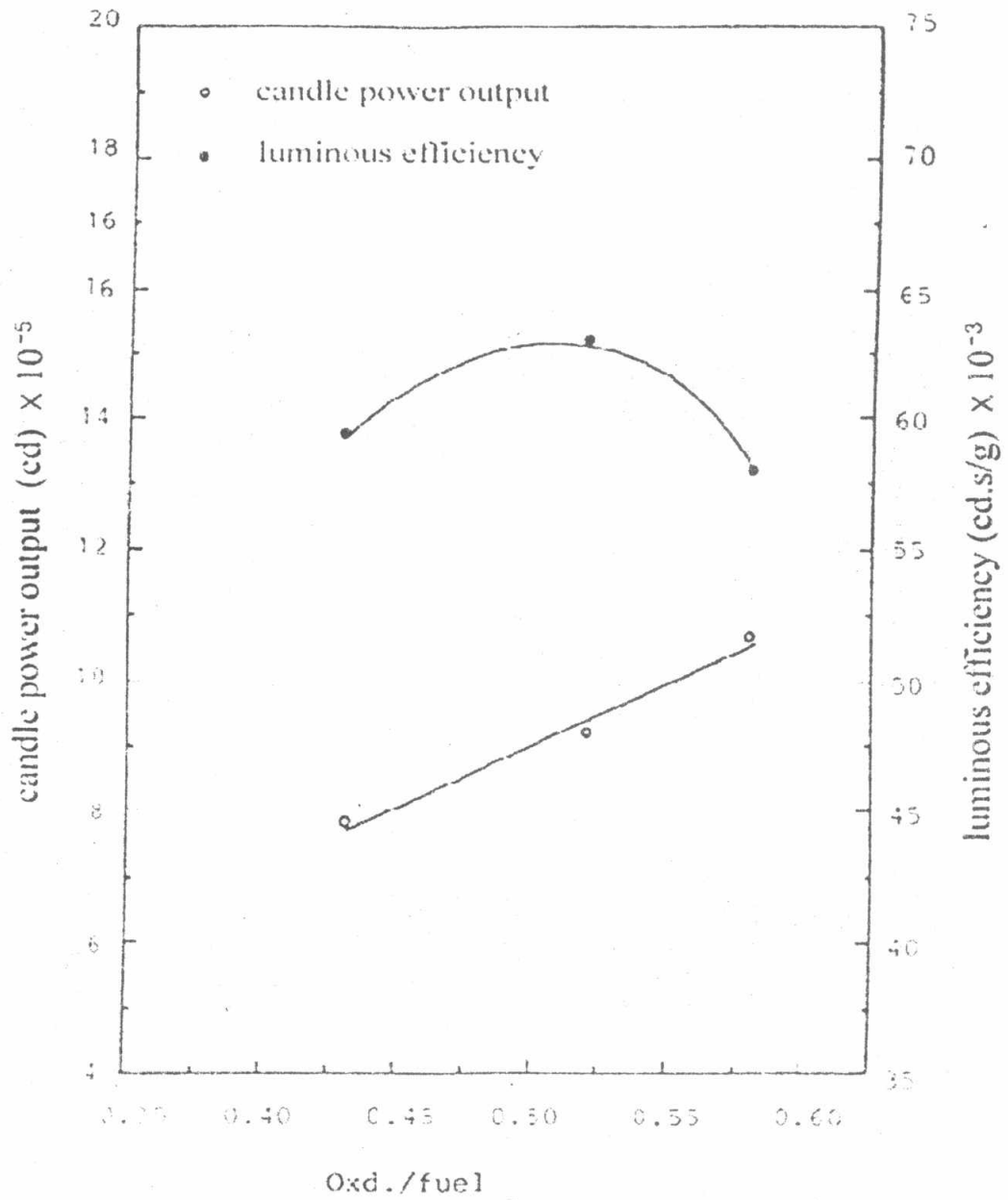


Fig. (3): Effect of varying the oxidizer to fuel ratio on candle power output and luminous efficiency for compositions containing sodium nitrate only.

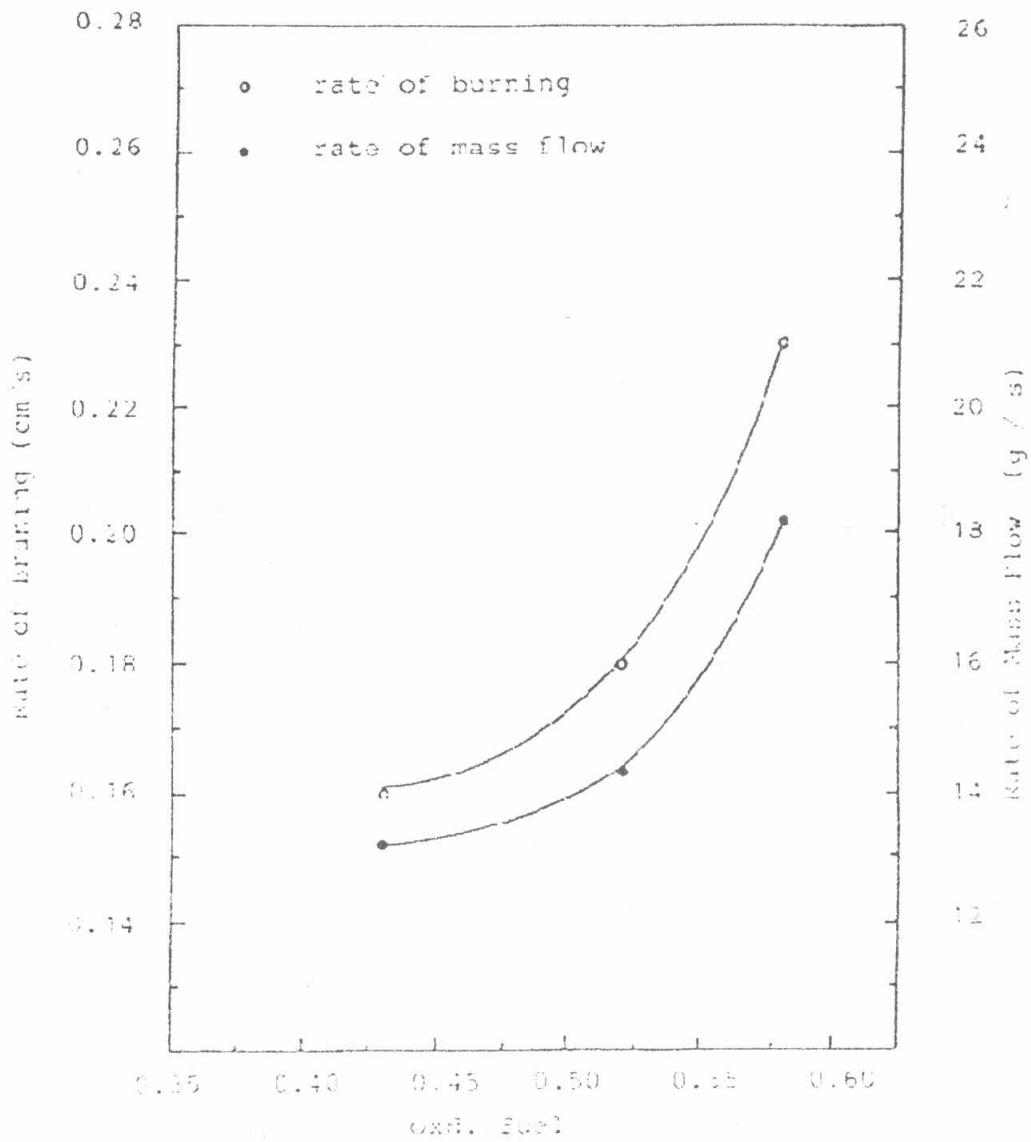


Fig. (4): Effect of varying the oxidizer to fuel ratio on rate of burning and rate of mass flow for compositions containing sodium nitrate only.