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FINE-CRYSTALLINE ALKALINE EARTH METAL PEROXIDES FOR OXIDE CATHO--ETC(U)
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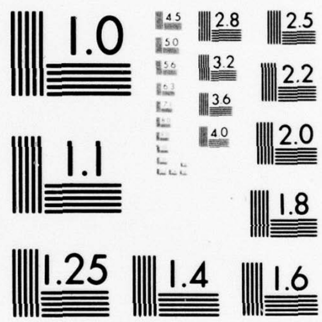
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By

Ye. A. Yepifantseva, T. G. Aryanina, et al

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By: Ye. A. Yepifantseva, T. G. Aryanina, et al

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В в	*В в*	V, v	Т т	*Т т*	T, t
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

FINE-CRYSTALLINE ALKALINE EARTH METAL PEROXIDES FOR OXIDE CATHODES

Ye. A. Yepifantseva, T. G. Aryanina, V. T. Redchenko, and S. A. Mikulin

The influence of reaction mixture temperature, concentration and rate of admixing initial solutions upon precipitate dispersion of calcium strontium and barium peroxides have been examined. A new method has been proposed for obtaining homogeneous fine-grained alkali-earth peroxides for oxide cathodes of luminescent tubes. It was found that fine-grained peroxides increase emission current and cathode emission homogeneity.

There are known advantages in the use of peroxides of calcium, strontium and barium in place of ternary carbonate for the development of an oxide layer on cathodes of fluorescent lamps [1-4]. However, peroxides in an oxide suspension in contact with organic solvents and varnish forming substances are less stable in comparison with carbonates. An improvement in the stability of an oxide suspension with peroxides was achieved by means of the replacement of the cellulose with polymers of methacrylic acid [1, 4], nevertheless any new step toward improvement of stability would be useful, especially for mass production.

In connection with this, there is much current interest in the study of the conditions of obtaining and the possibility of application in the production of oxide cathodes of fine-crystalline peroxides of calcium, strontium and barium of homogeneous granulometric composition. The use of such peroxides would make it possible to reduce considerably the duration of "grinding" of the solid phase of the oxide suspension in ball mills or even to replace "grinding" by simple mixing of the suspension.

More than once in the literature on oxide cathodes the question has been raised concerning the size of the grains of the initial ternary carbonate. Although it is noted [5] that there is no substantiated opinion of which geometry of carbonate particle is optimal, the influence of particle size on the emission capacity of the oxide cathode is not negated. One has to agree with the author of [5] that other circumstances are also important: the nucleus, processes of formation of cathodes within devices, the gaseous media, operating conditions of the cathodes, etc. It is considered [6] that, using a fine-crystalline initial ternary carbonate, it is easy to cut down the duration of "grinding" of the solid phase, and, consequently, the probability of contamination of the suspension with impurities from the material of the balls and the mill. Apparently in the process of "grinding" "splinters" of crystals also appear and the possibility of deformation of the crystal lattice following the "erosion" of the crystals is not excluded. This can influence the emission capacity of the cathode.

Many years of practical experience in the development of oxide cathodes shows that for the purpose of increasing the longevity of luminescent tubes it is necessary, after "grinding," to maintain the particle size of ternary carbonate at around 1 μm. Taking into account the chemical activity of peroxides and the increase in the surface thermodynamic potential with a reduction in crystal size [7], an optimal grain size of around 1.5 μm was established for oxide suspensions with peroxides. For ensuring the homogeneousness of the cathodes in respect to longevity, along with other factors the uniformity of oxide grain size is also important. Especially under conditions of mass production, when the length of time for processing of the cathodes is limited, if there are large grains present there is the possibility of the existance in the depth of the crystals of nondissociated barium peroxide as the most thermally stable component of the oxide layer. In the case of the presence of very small grains in the initial suspension after "grinding" a "dust" fraction appears which subsequently causes blackening of the ends of the fluorescent lamp.

In this work a method is described for obtaining fine-crystalline peroxides, in which the number of grains 1-2 μm in size should be no less than 80% in respect to the total number of particles, and the results are cited from the tests of such peroxides in the case of producing oxide cathodes.

In the literature on the peroxides of the alkaline earth metals there are no data on the influence of the conditions of synthesis on the degree of dispersion of precipitates. Having assumed that in the case of peroxides it is possible to be guided by the general regularities of crystallization of precipitates of compounds from aqueous solutions, a study was made of the influence of temperature of the reaction system, concentration and rate of pouring of the initial solutions on the degree of dispersion of precipitates of peroxides of calcium, strontium and barium.

The tests were conducted on a laboratory installation which was described earlier [8]. In all the tests the ratio of the volumes of poured solutions of salt, hydrogen peroxide and ammonia was maintained constant and was equal to 1:1:1. During the study of the influence of temperature and concentration of the solutions on the degree of dispersion of the peroxide precipitates the solutions were decanted at a rate of 2.8 ml/s. As is evident (Table 1), the temperature of the reaction mixture, the concentration of initial solutions (Table 2), and the rate of their decantation (Table 3) exerted a significant influence on the degree of dispersion of the precipitates of the resulting peroxides. For obtaining fine-crystallized peroxides of an assigned granulometric composition the optimal temperature intervals are -1 - +2, 8-10, and 5-7°C for the peroxides of calcium, strontium and barium respectively. The optimal rate of decantation of the initial solutions is a rate of 2.8 ml/s. The concentrations of the initial solutions of salt, hydrogen peroxide and ammonia were selected respectively:

12-15, 9-11, 6-9% when obtaining calcium peroxide, 15, 9 and 3.5% when obtaining strontium peroxide, and 6, 5 and 3% when obtaining barium peroxide.

Table 1

The influence of the temperature of the reaction mixture on the degree of dispersion of precipitates of peroxides

(1) Исходные соли	(2) Концентрации растворов, *вес.* %			T °C	(6) Получаемые перекиси	
	(3) соли	(4) перекиси водорода	(5) аммиака		(7) формула	(8) количество частиц с размерами 1—2 мкм по отношению к общему количеству частиц, %
$(CaNO_3)_2$	12	9	6	—2	CaO_2	80—85
	12	9	6	0		80
	12	9	6	1		80
	12	9	6	4		75
$Sr(NO_3)_2$	15	9	3,5	5	SrO_2	95
	15	9	3,5	10		90—95
	15	9	3,5	15		90
	15	9	3,5	20		80
$(BaNO_3)_2$	6	5	3	5	BaO_2	80—85
	6	9	3	10		80
	6	9	3	15		75
	6	9	3	20		75

Key: (1) Initial salts; (2) Concentrations of solutions, wt.%; (3) salt; (4) hydrogen peroxide; (5) ammonia; (6) Peroxides obtained; (7) Formula; (8) number of particles 1-2 μm in size in respect to the total number of particles, %.

Dehydration of the precipitated peroxides was done in an aqueous suspension with a ratio T:Zh=1:4 and temperature of 45-50°C. After washing, the precipitates were dried at a temperature of 110-120°C and residual pressure of 20-30 mm Hg for 3-4 hours.

On the basis of the resulting data a laboratory method was developed for obtaining fine-crystalline peroxides of calcium, strontium and barium for the oxidation of cathodes. The characteristics of test batches of peroxides obtained by this method are given in Table 4.

Table 2

The influence of concentration of solutions on the degree of dispersion of precipitates of peroxides

(1) Исходные соли	Концентрации растворов, *вес.* % (соотношение объемов 1:1:1) (2)			(6) Температура реакционной смеси, °C	(7) Получаемые перекиси	
	(3) соли	(4) перекиси водорода	(5) аммиака		(8) формула	(9) количество частиц с размером 1—2 *мкм* по отношению к общему количеству частиц, %
	12	9	6	−1—+2		80
$Ca(NO_3)_2$	15	11	9	−1—+2	CaO_2	(10) 85—90
	24	18	11	−1—+2		Кристаллы очень мелкие, плохо отделяются при фильтровании
	12	6	3	8—10		90—95
$Sr(NO_3)_2$	15	9	3,5	8—10	SrO_2	(11) 90
	30	17	7	8—10		Кристаллы очень мелкие, плохо отделяются при фильтровании
$Ba(NO_3)_2$	6	5	3	5—7	BaO_2	80—85

Key: (1) Initial salts; (2) Concentrations of solutions, wt.% (ratio of volumes 1:1:1); (3) salts; (4) hydrogen peroxide; (5) amonia; (6) Temperature of the reaction mixture, °C; (7) Peroxides obtained; (8) formula; (9) number of particles with a size of 1-2 μm in respect to the overall number of particles, %; (10) Crystals very fine, separated poorly with filtration; (11) Crystals very fine, separated poorly with filtration.

During the preparation of the oxide suspension on the basis of fine-crystalline peroxides of calcium, strontium and barium and zirconium dioxide the duration of "grinding" of the solid phase was reduced by three times and the number of balls in the mill reduced by five times. After the preparation of the cathodes the currents of thermal emission of the cathodes of the vacuum diodes were compared using the method of filament characteristics. Figure 1 shows the results, graphically illustrating the certain increase of current of emission in the case of a filament current of 250 mA (without "grinding" 15.6, with "grinding" 12.2 mA) and the high degree of emission homogeneousness of the cathodes which where oxidized by a suspension, prepared virtually without "grinding" of the solid phase.

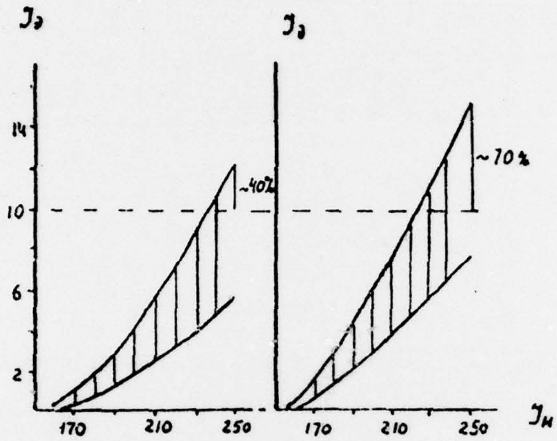

Figure 1. Filament characteristics of cathodes of vacuum diodes with $BaO_2:SrO_2:CaO_2$=50:30:20 mole % + 10 wt.% of ZrO_2:
a - with "grinding" of the peroxides; b - without "grinding" of the peroxides.

Testing of the new technology of preparation of an oxide suspension on a base of fine-crystalline peroxides of alkaline earth metals is continuing. The first test batch of fluorescent lamps with cathodes oxidized by fine-crystalline peroxides showed a high degree of stability: in lamps LB-30 with the LG-1k luminophore after 5000 hours of burning the light yield comprised 53 lm/W, while using GOST 6825-70 according to Table 4 after 4000 hours of burning in lamps LB-30-4 with the LG-10 type luminophore a light yield of no less than 45.5 lm/W is acceptable.

Table 3

The influence of rate of pouring of solutions on the degree of dispersion of precipitates of peroxides

(1) Исходные соли	(2) Концентрация растворов, вес. %			(6) Температура реакционной смеси, °C	(7) Скорость сливания растворов, мл/сек	(8) Получаемые перекиси	
	(3) соли	(4) перекиси водорода	(5) аммиака			(9) формула	(10) количество частиц с размерами 1—2 мкм по отношению к общему количеству частиц, %
$Ca(NO_3)_2$	12	9	6	−1—+2	5,7	CaO_2	80
	12	9	6	−1—+2	2,8		75—80
	12	9	6	−1—+2	2,0		60
	12	9	6	−1—+2	0,8		40
$Sr(NO_3)_2$	15	9	3,5	8—10	5,0	SrO_2	90—95
	15	9	3,5	8—10	2,8		87
	15	9	3,5	8—10	2,0		80
	15	9	3,5	8—10	2,0		75
	15	9	3,5	8—10	0,8		70
$Ba(NO_3)_2$	6	5	3	5—7	5,0	BaO_2	85
	6	5	3	5—7	2,8		80
	6	5	3	5—7	2,0		75
	6	5	3	5—7	0,8		70

Key: (1) Initial salts; (2) Concentration of solutions, wt.%; (3) salt; (4) hydrogen peroxide; (5) ammonia; (6) Temperature of the reaction mixture, °C; (7) Rate of pouring of solution, ml/s; (8) Peroxides obtained; (9) formula; (10) number of particles with a size of 1-2 μm in respect to the overall number of particles, %.

Table 4

Characteristics of test batches of peroxides

Перекиси	Гранулометрический состав: размер зерен, мкм	количество частиц данного размера по отношению к общему количеству частиц, %	Содержание основного вещества, %	Содержание примесей, %: азота общего	хлоридов	железа	тяжелых металлов сероводород. группы (Pb)	калия и натрия
	1—2	90						
SrO_2	<1	2	97,7	0,005	0,001	0,0005	0,0005	0,0021
	>2	8						
	1—2	80						
CaO_2	<1	5,6	90	0,003	0,005	0,0005	0,0005	0,022
	>2	14,4						
	1—2	80						
BaO_2	<1	6	97	0,003	0,005	0,0001	0,0003	0,009
	>2	14						

Key: (1) Peroxides; (2) Granulometric composition; (3) grain size, μm; (4) number of particles of the given size in respect to the overall number of particles, %; (5) Content of main substance, %; (6) Content of admixtures, %; (7) nitrogen overall; (8) chlorides; (9) iron; (10) heavy metals of the hydrogen sulfide group (Pb); (11) potassium and sodium.

CONCLUSIONS

1. A method has been developed for obtaining fine-crystalline peroxides of alkaline earth metals, which are homogeneous in granulometric composition, for the oxide cathodes of fluorescent lamps.

2. In an example of an oxide suspension on a base of fine-crystalline peroxides of alkaline earth metals with the composition 50:30:20 mole %=BaO_2:SrO_2:CaO_2+10 wt.% ZrO_2 a correlation was revealed between the size of the grains and the duration of "grinding" of the solid phase of the suspension, on the one hand, and the thermal emission of oxide cathodes on the other.

Submitted 3.8.1971

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