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Application of arsenic to electrophotoreceptors

Hideki Kina, Toshiyuki Iijima and Yasuo Nakaura
Fuji Electric Co. Ltd, 2666 Tsukama Matsumoto, Nagano 390, Japan

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Arsenic has been applied to many electronic devices such as electrophotoreceptors, gallium arsenide (GaAs) semiconductors and solid-state image pick-up devices. For electrophotoreceptors selenium–arsenic (Se–As) alloys are coated onto the conductive substrate of the receptors. Arsenic is mostly used in electophotoreceptors in electronic devices.

During the coating process, a part of the gaseous arsenic is released through an exhaust system. In order to avoid arsenic being discharged to the atmosphere, bag filters and high-efficiency particulate air filters are set before the exhaust port. Any arsenic which still exists in the waste water after washing tools and jigs from the coating process is collected by sedimentation before discharging.

The Ames salmonella/microsome plate test for As_2Se_3 indicated no mutagenic activity under the test system used. For the safety of workers engaged in arsenic-related jobs, they received a medical examination once every six months. No negative trends from the examination was found in 428 men who received the examination from Autumn 1980 to Spring 1987.

Keywords: Arsenic, selenium, electrophotoreceptor, safety, pollution, Ames test.

INTRODUCTION

Arsenic applied to electrophotoreceptors is generally used in the form of an As:Se compound or alloy such as As_2Se_3. These alloys have excellent properties as electrophotoreceptors, e.g. high sensitivity and durability.

In this paper, we will first explain the outlines of the function of an electrophotoreceptor and the features of As_2Se_3 photoreceptors, then we will describe the production process of As_2Se_3 photoreceptors and pollution control methods. Finally we will show data from Ames salmonella/microsome plate tests and medical examinations for workers.

ELECTROPHOTORECEPTORS

Electrophotoreceptors have photoelectric transfer characteristics,[1,2] which are applied to PPCs (Plain Paper Copiers) and LBPs (Laser Beam Printers) for xerographic processes. The function of photoreceptors is nearly equivalent to films in cameras. The main difference between them is that a film can only be exposed once, while photoreceptors can be used repeatedly, and no chemical reactions are involved in processing. It is a dry photoelectric process.

Figure 1 shows several kinds of photoreceptors which are cylindrical and have different diameters and lengths according to their function as copiers or printers. It also shows a cross-section of an As_2Se_3 photoreceptor, in which the thickness of the As_2Se_3 photoreceptive layer deposited on an aluminum substrate is about 60 μm. Historically, selenium has been used for photoreceptive materials, but nowadays there exist several kinds of photoreceptive materials such as Se:Te species, As_2Se_3, various OPCs (Organic Photoconductors), zinc oxide and cadmium sulphide. Their characteristics are shown in Table 1. As_2Se_3 photoconductors have a long life and high sensitivity, particularly because their surface hardness is high, as shown in Fig. 2, and they have photosensitivity even at longer wavelength as shown in Fig. 3.

The expected shares of photoreceptor types used in 1987 have been estimated by Data Quest to be Se:Te species, 48%; OPCs, 43%; Se:As species, 8%; others, 1%. About 20 tonnes of arsenic was used for production of As_2Se_3 photoreceptors in 1987.

PRODUCTION OF As_2Se_3 PHOTORECEPTORS

As_2Se_3 photoreceptors are produced by vacuum-coating methods. Vitreous As_2Se_3 pellets and aluminum piping are used in the coating process.

Figure 4 shows a cross-section of a planetary coating machine. Aluminum pipes are mounted to the mandrels

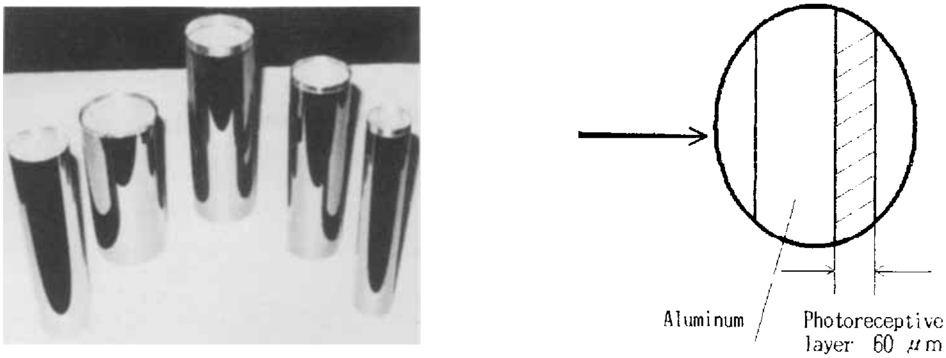

Figure 1 Construction of photoreceptor.

Table 1 Features of photoreceptive materials

Property	ZnO	CdS	OPC	Se:Te	Se:As
Life	D	B	C	A	A
Sensitivity	C	C	C	B	A
Fatigue	D	C	C	B	C
Toxic properties	B	D	B	C	C
Cost	A	B	A	B	C
Production in 1987, million tonnes			3.8	4.3	0.7

Key: A, excellent; B, good; C, fair; D, poor to insufficient.

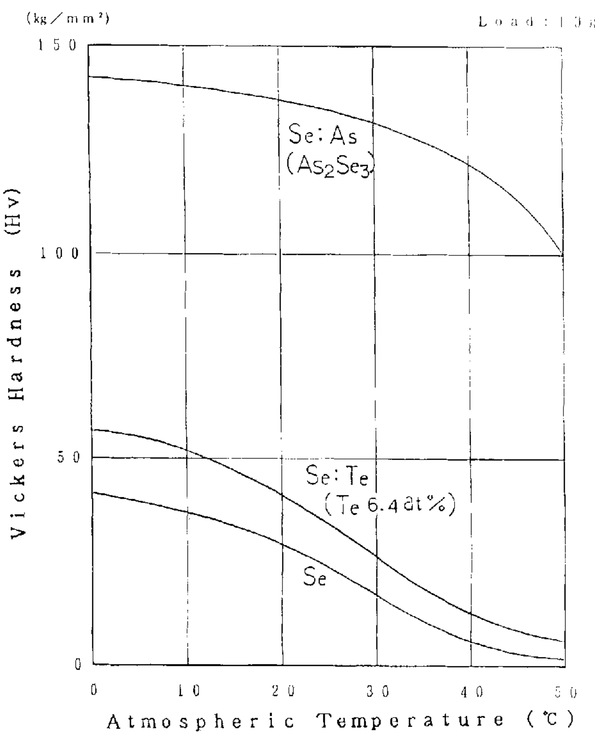

Figure 2 Surface hardness of photoreceptors.

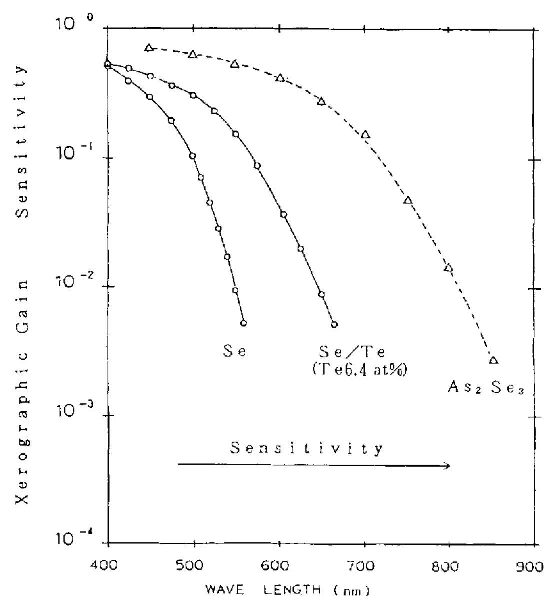

Figure 3 Sensitivity of photoreceptors.

and the As_2Se_3 material is evaporated to become deposited on the aluminum pipes.

In coating processes, gaseous arsenic must be collected before discharging to atmosphere, and waste water which contains arsenic after washing tools and jigs for the coating process must be treated before discharging.

Figure 5 shows a pollution control method for gaseous arsenic from coating processes. During the coating process, part of the gaseous arsenic is released through the exhaust system. It is collected in vacuum pumps and oil mist collectors. The exhausted gas runs through the bag filters and the high-efficiency particulate air (HEPA) filters to the atmosphere. When coating is completed the bell jar of the coating machine will be opened. The arsenic fume remaining is also ex-

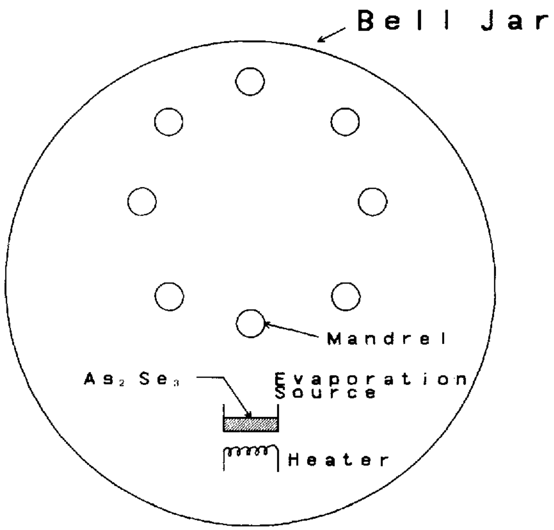

Figure 4 Cross-section of coating machine. Conditions: evaporation temperature of material 370–450°C; vacuum 10^{-4}–10^{-6} torr.

hausted and arsenic particles collected using the same filter system. Used filters, used vacuum oil and oil collected in the oil mist collector are treated by industrial waste control companies by lawful means.

Figure 6 shows a pollution control method for waste water containing arsenic from coating processes. It is treated by a sedimentation method. Arsenic precipitant is treated by industrial waste control companies by the same method mentioned above. After sedimentation

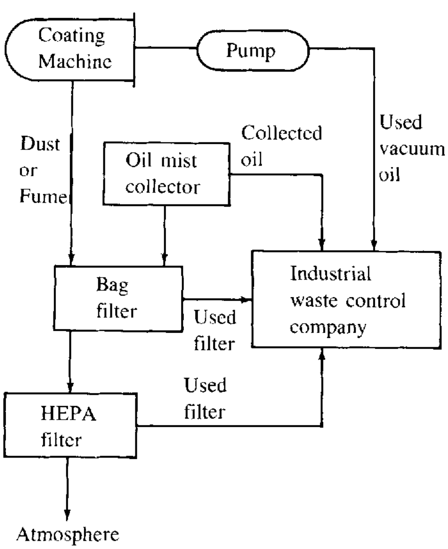

Figure 5 Pollution control methods for arsenic exhaust gas during vacuum coating process. HEPA, high-efficiency particulate air.

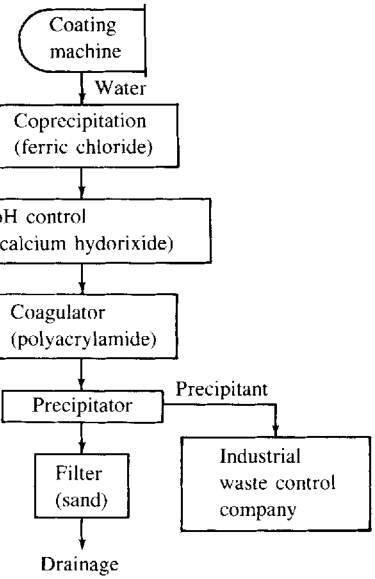

Figure 6 Pollution control methods for arsenic in waste water during vacuum-coating process.

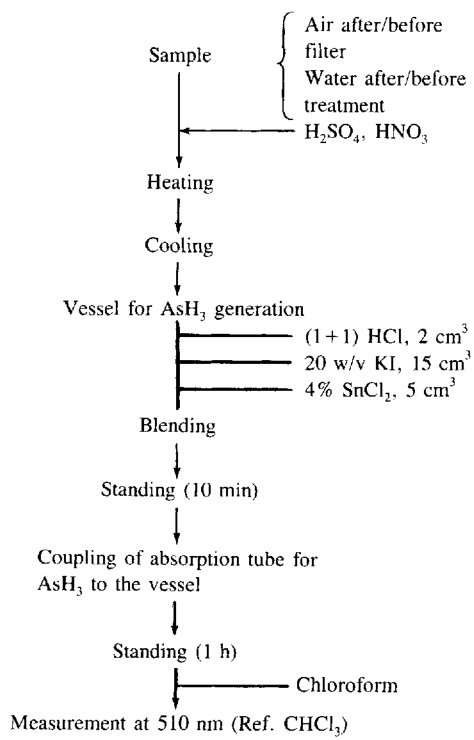

Figure 7 Diethyldithiocarbamic acid absorptiometric method for determination of arsenic concentration (by Japan Industrial Standard K0102).

the water is discharged through a sand filter to drainage.

In order to investigate the capability of arsenic collection by the above pollution control method, we determined the arsenic concentration in the exhausted gas and waste water before/after the filters or treatment by the diethyldithiocarbamic acid absorptiometric method[3] shown in Fig. 7.

Arsenic concentration determined in exhaust gas is below the detection limit (0.003 mg m^{-3}). This indicates that arsenic is sufficiently collected by the vacuum pumps and oil mist collectors. Therefore we tried an intensive experiment, in which gas from the exhaust duct is sampled and analysed before and after passing through both a bag filter and an HEPA filter. This indicates that arsenic is still sufficiently collected by the filtering system used. The arsenic in waste water is also sufficiently collected by the sedimentation. The results are shown in Tables 2 and 3.

Table 2 Arsenic concentration of exhaust gas as intensive experiment

	Arsenic concentration (mg m^{-3})	
Experiment number	Before filter	After filter
1	0.146	<0.003
2	0.076	<0.003
3	0.044	<0.003
4	0.367	<0.003

Table 3 Arsenic concentration in waste water

	Arsenic concentration (mg m^{-3})	
Experiment number	Before treatment	After treatment
1	0.127	<0.001
2	0.101	<0.001
3	0.200	<0.001
4	0.166	<0.001

AMES TEST FOR As_2Se_3

We entrusted the Hatano Research Institute with the Ames salmonella/microsome plate test for As_2Se_3. The test flow chart is shown in Fig. 8. Tables 4 and 5 indicate no mutagenic properties under the test system used.

Table 4 Result of Ames test (I)

		Revertants/plate (mean)								
As_2Se_3 dose/plate (μg)	S−9	TA100			Ta1535			WP2 uvrA		
5000	−	123	120	(122)	18	23	(21)	15	12	(14)
1000	−	116	114	(115)	25	23	(24)	13	14	(14)
500	−	123	121	(122)	18	24	(21)	15	17	(16)
100	−	107	114	(111)	20	21	(21)	14	16	(15)
50	−	117	111	(114)	20	23	(22)	12	12	(12)
10	−	114	120	(117)	19	19	(19)	13	10	(12)
0	−	115	121	(118)	18	22	(20)	12	10	(11)
5000	+	115	134	(125)	20	17	(19)	15	14	(15)
1000	+	131	129	(130)	17	19	(18)	17	17	(17)
500	+	115	120	(118)	14	14	(14)	19	18	(19)
100	+	126	115	(121)	15	18	(17)	16	15	(16)
50	+	131	134	(133)	19	20	(20)	20	17	(19)
10	+	125	120	(123)	15	16	(16)	15	17	(16)
0	+	123	130	(127)	17	16	(17)	12	16	(14)
Positive control	−	AF2 (0.01 μg)			ENNG (5 μg)			AF2 (0.04 μg)		
		632	649	(641)	116	122	(119)	170	154	(162)
	+	2AA (0.5 μg)			2AA (1 μg)			2AA (10 μg)		
		357	401	(379)	87	94	(91)	192	188	(190)

Abbreviations: AF2, 2-(2-furyl)-3-(5-nitro-2-furyl) acrylamide; 2AA, 2-aminoanthracene; ENNG, *N*-ethyl-*N*-nitro-*N*-nitrosoguanidine.

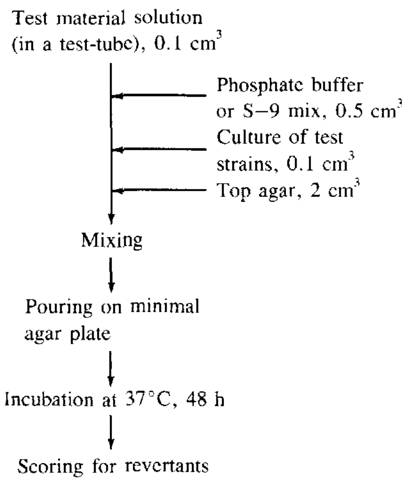

Figure 8 Ames salmonella/microsome plate test for As_2Se_3 (Hatano Research Institute).

MEDICAL EXAMINATION OF WORKERS

Concerning the usage of As_2Se_3, there is no legal duty in Japan for medical examination of workers. However, our company has been carrying out medical examinations for workers as a precautionary measure. The medical symptoms and tests listed below were considered, being those concerned in the use of As_2O_3 regulated by Japanese labor laws.

(1) Abnormality of nasal mucous membrane.
(2) Stomatitis.
(3) Symptoms of the respiratory organs.
(4) Constipation.
(5) Weight loss.
(6) Diarrhea.
(7) Paresthesia.
(8) Cough.
(9) Loss of appetite.
(10) Observation of nasal septum perforation.
(11) Dermatitis.
(12) Hyperkeratosis.
(13) Pigmentation.
(14) Depigmentation.
(15) Urinary urobilinogen.
(16) Specific gravity of blood.
(17) Hb, GOT, GPT, AL–P.

No negative trends were found over a seven-year period for 428 workers.

Table 5 Result of Ames Test (II)

		Revertants/plate (mean)								
As_2Se_3 dose/plate (μg)	S–9	TA98			TA1537			TA1538		
5000	–	21	24	(23)	10	9	(10)	21	20	(21)
1000	–	23	24	(24)	8	5	(7)	19	23	(21)
500	–	20	19	(20)	10	7	(9)	24	24	(24)
100	–	21	22	(22)	5	6	(6)	21	23	(22)
50	–	25	30	(28)	7	4	(6)	19	19	(19)
10	–	19	24	(22)	10	9	(10)	18	20	(19)
0	–	25	21	(23)	5	8	(7)	20	24	(22)
5000	+	36	36	(36)	12	13	(13)	20	25	(23)
1000	+	37	35	(36)	11	12	(12)	24	26	(25)
500	+	40	41	(41)	10	7	(9)	23	20	(22)
100	+	38	41	(40)	13	12	(13)	25	26	(26)
50	+	42	44	(43)	9	11	(10)	24	25	(25)
10	+	35	40	(38)	12	10	(11)	22	22	(22)
0	+	42	40	(41)	10	11	(11)	23	25	(24)
	–	AF2 (0.02 μg)			9AA (50 μg)			4NOPD (1 μg)		
Positive		135	127	(131)	94	101	(98)	151	142	(147)
control	+	2AA (0.5 μg)			2AA (1 μg)			2AA (0.5 μg)		
		139	145	(142)	53	48	(51)	153	160	(157)

Abbreviations: AF2, 2-(2-furyl)-3-(5-nitro-2-furyl) acrylamide; 2AA, 2-aminoanthracene; 9AA, 9-aminoacridine; 4NOPD, 4-nitro-*o*-phenylenediamine.

CONCLUSION

During the electrophotoreceptor vacuum-coating process, arsenic in air or in water is collected sufficiently by air filters or by sedimentation and filtering.

As_2Se_3 is not mutagenic so far as is shown by the Ames salmonella/microsome plate test. No abnormality on medical examination of workers was found.

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REFERENCES

1. Schaffert, R M *Electrophotography*, Focal Press Ltd, London, 1975, p27
2. Carlson, C F US Patent 2221176 (1938, 1940); US Patent 2297691 (1939, 1942), US Patent 2357809 (1940, 1944)
3. Japan Industrial Standard K0102