The Change of Pearl Colors by the Irradiation with γ-ray or Neutron ray[*]

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ABSTRACT

Pearls produced either in pearl oyster or in fresh-water mussel change their colors into black by the irradiation with either γ-ray or neutron rays. In this coloration, blackish pigment are found chiefly in the inserted nuclei of the pearls produced in fresh-water and of marine mollusks and also in the pearl layer of pearls produced in fresh-water mussel, but scarcely be found in those of the pearl layer of the pearls produced in Japanese pearl oyster. The insertion nucleus is made of pearl layer in shell of fresh-water clam.

Both the pearl layer in shell or in pearl of fresh-water clam easily change its color from original to black by the irradiation. In order to clarify the mechanism of the coloration, the colored pearls were observed using the chemical and physical methods.

In physical observation, in the colored pearls examined submicroscopically using electron microscope and x-ray diffractometer and heat-effects, no physical differences can be found before and after the irradiation (Figure 1, 2, and Table II).

In chemical observation, the shell of fresh-water clams contain comparatively larger amounts of Mn than those of marine ones (Table III).

Those results shown in Table III suggest that the greater part of Mn in the shell of fresh-water clam really exists and its oxides caused by the irradiation are possibly due to the blackish color.

It is well known that the common colors of pearl such as white, silver, pink, cream, and gold are changed into black or blue by the irradiation of either γ-ray

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from Co[60] or neutron rays from the atomic pile (TSUJII, HORIGUCHI, and OKADA, 1959). In such a case, the pearls produced in fresh-water mussel changed into much deeper black than the pearls produced in Japanese pearl oyster did. This may be due to the following reasons: in the case of the pearls from fresh-water mussel, not only the pearl layer but also the inserted nucleus change into black color, but with the pearls from Japanese pearl oyster, the pearl layer does not possibly change into black while the inserted nucleus becomes black, which can be observed through the uncolored thin pearl layer.

In this paper, the correlation between the degree of coloration and the irradiated doses, and the mechanism of this coloration is described.

MATERIALS & METHODS

The pearls of common colors produced in Japanese pearl oyster, *Pteria (Pinctada) martensii* (DUNKER) and in fresh-water mussel, *Hyriopsis schlegelii* (v. MARTENS), shell of the bivalves, insertion nuclei, $MnCO_3$ were subjected to irradiation.

The irradiation of γ-ray from Co[60] were conducted at the Tokai Laboratory of Japanese Atomic Energy Research Institute and also the Nagoya Reseacrh Institute of Industrial Technology. The irradiation with neutron was performed in the pile of JRR-1 in the Tokai Laboratory of Japanese Atomic Energy Research Institute.

Before and after the irradiation, the color of pearls were measured with the automatic spectrophotometer (Shimazu RC-1), and the submicroscopic structures of pearl layer and insertion nucleus were examined with the electron microscope and by the x-ray diffractometer respectively. For the electron microscopical study, two-step replicas of the surface of irradiated pearl and insertion nucleus were prepared by acethylcellulose-carbon instead of plastics (FUKAMI, 1958). Carbon films were vaporized on the sheet, which was dissolved away in methyl acetate. As for the x-ray diffractometical observation, the fine powder of pearl layer of the blackened pearl was prepared, by separating the pearl layer from the inserted nucleus and grinding it down into fine powder in the agata-morta, and it was analysed by x-ray diffractometer: under such experimental conditions as copper K_2 radiation ($\lambda = 1.5418$), 30 kv, 15 mA. Scanning speed 2/min., time constant 4 seconds, slit system $1°-1°-0.4°$.

RESULTS

I . *Relations between the degree of coloration and irradiation doses*

The color of pearl produced in fresh-water mussel becomes black, proportionately deeper with irradiated doses. The same relation was observed with the inserted nucleus of the pearl produced in pearl oyster. In the latter case, and when the thickness of the pearl layer is constant, the color of pearl became darker, proportionately with the irradiated doses, although the nacreous layer was not possibly colored by the irradiation. But, thicker the pearl layer, the darker color, which could be observed through the uncolored pearl layer was reduced. The effects of

Table I. Relationship of Various Doses of γ-and Neutron Rays with Coloration Highly Qualified for the Market.

		Irradiation Time	Doses	Quality
Neutron Irradiation	1 hr. Irradiation	40 KW 1hr.	5×10^{14} neutron/cm^2	—
	1 Week Irradiotion	40 KW 15–20 hrs.	1×10^{16} //	—
	1 Month Irradiation	40 KW 60–80 hrs.	4×16^{16} //	+

	Irradiation Time	Doses/hr.	Doses	Quality
γ-Irradiation	1 hr.	9.3×10^4	9.3×10^4	—
	16 hrs.	9.3×10^4	1.5×10^6	—
	12 hrs.	1.7×10^6	2.0×10^7	+
	60 hrs.	1.7×10^6	1.0×10^8	+

various doses of neutron ray and γ-ray on the coloration of pearls are shown in Table 1.

From the experimental results it is apparently shown that the coloration reaches its maximum at 2×10^7, further irradiation has no effect for coloration. But, the black pearls caused by neutron irradiation at the dosage of 4×10^{16} neutron/cm^2, became radioactive, and the activity was about 200 $m\gamma$., measured through capsel in which pearls were kept during the irradiation in the pile. These radioactive pearls were decomposed into calcium oxalate, proteins, conchiolins, rare earth elements and $BaCO_3$, and among these fractions more than 93% of the total radioactivity was recognized in the fraction of calcium oxalate.

The patterns of coloration change are shown in Figure 1. From this figure, it is clear that the pearls produced in fresh-water mussels and insertion nucleus changed into deeply black. Since the pearl layer formed in the Japanese pearl oyster was not visibly colored by irradiation as mentioned above, the color or pearl which could be observed through thin pearl layer was much lighter than
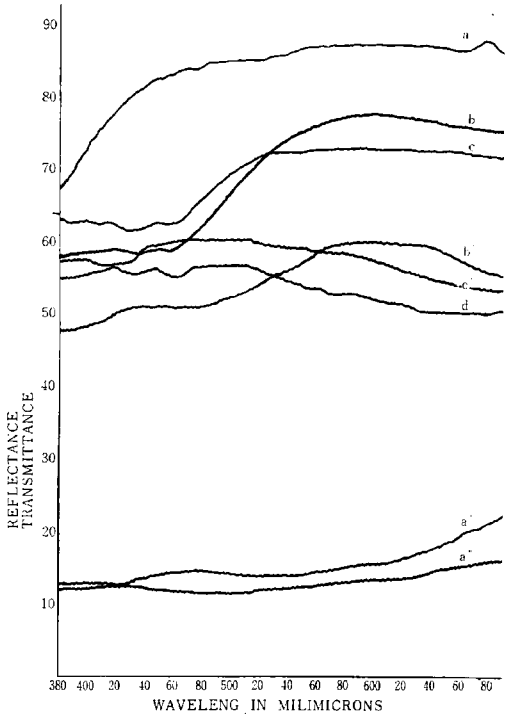

Figure 1. Spectrophotometric reflectance curve of the Pearls.
a- the reflectance curve of the insertion nucleus; a'-the curve after irradiation of a; a''- the same curve of insertion nucleus after stained by chemical reagent.
b- the reflectance curve of the pearl (No. 1); b'-the curve after irradiation of the pearl (No. 1).
c- the curve of the peral (No. 2); c'- the curve of after irradiation.
d- the reflectance curve of natural black peari.

that of insertion nucleus.   The curves of these colored pearls produced by irradiation closely resembles to those of natural black pearls.

II. *Observation on the submicroscopic structure of colored pearls*

Submicroscopic observations on the surface and transverse section of blackened pearl and inserted nucleus were made with the electron microscope.   In these preparations, the author could not find any visible changes which produced by the radiation (Figure 2).

The fine powder of irradiated pearls was analysed by x-ray diffractometer. The result is shown in Table II.   The difference in the intensity between the

Fig. 2. The electron microscopic picture of the laminary structure of the blakened insertion nucleus
×2,500

Table II. X-ray Powder Diffraction of the Pearl Layer.

Before Irradiation		After Irradiation	
d (Å)	I	d (Å)	I
3.41	24.0	3.42	8.6
3.29	13.5	3.30	4.0
2.88	9.0	2.88	2.8
2.71	35.0	2.72	13.6
2.49	15.0	2.49	5.2
2.41	6.0	2.42	1.0
2.38	16.5	2.38	5.6
2.20	5.0	2.20	0.8
2.11	5.0	2.11	1.8
1.98	12.0	1.98	4.8
1.82	8.0	1.82	2.0
1.75	16.5	1.74	5.6
1.73	9.5	1.73	3.0
1.70	3.0		
1.56	3.0		
1.50	3.0		
1.44	3.0		
1.41	5.5	1.41	1.0
1.36	5.0		

spacing of the lattices before and after irradiation as is shown in this table may be due to the lowering performance of the coolidge tube.   This assumption can be justified not only by the fact that the intensity decreased in constant ratio and without any remarkable difference with the location in between each spacing of the lattices, but by the decline in the background.

From these results, the author assumes that no difference are observed from the physical and crystalogical points of view.

Of other factors which can be assumed to be involved in the mechanisms of the coloration, it seems possible that the change in color should be caused by the change of the atoms in the lattices (SAKIGAWA, 1957).   In order to make this assumption clear, the blackened pearls were kept at 100 °C for 10–15 minutes.   The black color slightly decreased but still retained the color even after this treatment. This excludes the possibility of this assumption.

Another possible assumption is the heat-effects by irradiation, since pearls change into black when they are kept under the condition of more than 300 °C.

This may be due to the fact that the protein matrix in the pearl layer is burnt black. But, the pearls subjected to the irradiation of γ-ray of Co^{60} and neutron-ray in atomic pile were under the condition below 60°C. At this temperature, the pearl colore can never be changed under usual conditions.

III. *The difference in the mineral components between the pearls from fresh-water mussels and those from pearl oyster*

As mentioned above, the author could not find any difference from physical points of view in the pearls before and after irradiation. One of the author's co-workers, HORIGUCHI (1959), measured the mineral components of the shell of fresh-water mussel and that of marine mollusks. The results are shown in Table III. From the table, it is clear that the Mn content in the pearl layer in pearl oyster

Table III. Mn, Fe, Mg, Zn and Cu Contents of theShell of ShellZsh.
(from HORIGUCHI, 1959)

Species	Mn (p.p.m.)	(Fe (p.p.m.)			Mg (p.p.m.)	Zn (p.p.m.)	Cu (p.p.m.)
		Acid in-soluble	Acid soluble	Acid soluble Fe^{+++}			
Pteria (Pinctada) martensii (DUNKER)							
Periostracum & prismatic layer	75–107	147–224	238–273	149–183	3,873–4,014	21	2
Nacreous layer	1– 10	4– 10	18– 21	5	121–137	2	1
Pteria margaritifera (LINÉ)							
Periostracum & prismatic layer	58– 90	47– 51	106–107	39	3,215–3,439	7	1
Nacreous layer (black)	54– 76	6– 7	25– 27	2– 3	124	1	1
Nccreous layer (silver)	9– 37	3– 4	10– 11	3– 4	122–158	3	1
Pteria pengin (RÖDING)							
Periostracum & prismatic layer	4– 5	28– 29	44– 45	4– 5	1,382–1,658	4	1
Nacreous layer	1– 2	5– 6	20– 21	5– 6	85– 159	1	1
Lamprotula sp.							
Whole shell	246–284	8– 9	8– 11	8– 11	trace	1	2
Hyriopsis schlegelii (v. MARTENS)							
Nacreous layer	268–354	19– 20	18– 28	10– 12	trace	1	2
Corbicula sp.							
whole shell	14– 15	24– 27	74– 84	47– 52	29	1	1
Prismatic layer		27	22	10			
Meretrix meretrix lusora (RÖDING)							
whole shell	4– 7	26– 27	73– 79	55– 57	49 55	1	
Prismatic		11	5	1			
Venerupsis semidecussata (REEVE)							
Whole shell	13– 16	15– 16	68– 72	53– 62	60	3	1
Prismatic layer		trace	46	25			
Tridacna (Chaemetrachea) sp..							
Whole shell	trace	26– 28	12– 24	5– 6	102	1	1
Haliotis discus REEVE							
Whole shell	2– 3	36– 48	49– 50	16– 18	204	4	1
Nacreous layer		3	9	4		1	

is only about 1/40 of that in the fresh-water mussel, but no remarkable difference in the other mineral elements could be found between shell of fresh-water mollusks and that of marine ones. And he assumes that the $MnCo_3$ in pearl layer should be oxidized into a black substance by irradiation.

By histo-cytochemical methods the author unsuccessfully tried the distribution of Mn in pearl layer of fresh-water mussel, to see whether it exists in $CaCo_3$ or in organic matrix; the $CaCo_3$ and conchiolin which had been purificated from shell, were exposed to radiation, but no visible change was detected. Therefore, it is reasonably assumed that Mn combined with one of these might have been separated in the course of purification.

<div align="center">REFERENCE</div>

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