

Effects of a Gelatin Coating on the Shelf Life of Salmon

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This study was conducted to investigate the efficacy of using a coating of gelatin extracted from refiner discharge to extend the shelf life of salmon during cold storage (5°C). Relative percentage of moisture loss in gelatin-coated salmon during cold storage was less than that of uncoated salmon. The treatment of salmon with gelatin reduced volatile basic nitrogen (VBN) formation throughout the entire storage period. Measurements of the peroxide value (POV), fatty acid composition, and (20:5n-3+22:6n-3)/16:0 ratio during cold storage indicated that the coating of salmon with gelatin from refiner discharge effectively suppressed lipid oxidation over the entire storage period. The extent of sensory color change during cold storage was less in the gelatin-coated than in the uncoated salmon. From the results of chemical measurements, such as relative moisture content, VBN, POV, fatty acid composition, (20:5n-3+22:6n-3)/16:0 ratio, and sensory color change, the conclusion was made that the coating treatment of salmon with refiner discharge gelatin effectively suppressed moisture loss, lipid oxidation, and color deterioration over the entire storage period.

Key words: Salmon, Refiner discharge, Refiner discharge gelatin, Surimi, Seafood by-products

Introduction

Chemical oxidation of lipid and color, loss of essential fatty acids, and microbial changes during distribution and storage of seafoods lower the quality of the product. Cold storage does not always completely suppress the deterioration of seafood quality because reactions leading to oxidative and microbial changes can proceed under chilled storage conditions (Haard, 1992; Jeon et al., 2002). For these reasons, synthetic preservatives such as antioxidants, chelating agents, and antimicrobial compounds may be added to seafood products to improve their shelf life. However, growing consumer demand for seafoods devoid of synthetic antioxidants and preservatives has focused efforts on the discovery of natural preservatives or new methods for extending shelf life (Jeon et al., 2002).

Gelatin, commonly manufactured from land animal by-products, has been proposed for use as a coating on meat products (Antoniewski et al., 2007; Klose et al., 1952). In gelatin-coated meat products, water loss and the oxidation of myoglobin and lipids would be slowed and shelf life would be extended because the gelatin matrix is thought to act as a barrier to water and oxygen (Antoniewski et al., 2007). Today's health-conscious consumers, however, are reluctant to try gelatin extracted from land animals because of the recent outbreaks of bovine spongiform encephalopathy or foot-and-mouth disease (Kim and Park, 2004). Therefore, raw materials from fishery products are receiving new attention as a consumer-friendly source of gelatin coating.

Refiner discharge is a good resource for extracting gelatin because it accounts for approximately 4%-8% of the whole fish consumed during surimi processing (Park, 2006; Wendel, 1999), and it contains a significant amount of collagen (Morrissey et al., 2000). However, the use of surimi refiner discharge as a

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food source for humans has not been widely studied. Most refiner discharge is conventionally used to produce fish meal and fertilizer or directly discharged into estuaries, resulting in environmental pollution (Ciarlo et al., 1997). Thus, new challenges exist to identify methods to upgrade the processing of waste to food-grade ingredients such as gelatin.

Some efforts have previously been made to use a gelatin coating to extend the shelf life of various meat products, such as beef (Antoniewski et al., 2007), pork (Antoniewski et al., 2007; Marggrander and Hofmann, 1997), chicken (Antoniewski et al., 2007), and fish (Antoniewski et al., 2007; Lopez-Caballero et al., 2004; Qu et al., 2001; Zhang et al., 2007). However, these studies were limited to gelatin obtained from the skin and bone of land animals and fish, and did not use gelatin from refiner discharge.

The objective of this study was to investigate the efficacy of using gelatin coating obtained from refiner discharge to extend the shelf life of salmon during cold storage (5°C).

Materials and Methods

Materials

Salmon, *Oncorhynchus keta*, with a body length of 69-74 cm, was purchased from Wooyoung Fisheries Co., located in Busan, Korea, in October 2005.

Refiner discharge, a by-product of surimi processing of Alaska pollock, was provided by a commercial surimi processing plant (Trident Seafood Co., Warrenton, OR, USA) in January 2006. Gelatin was extracted from the refiner discharge using hot water, according to the method of Park (2006).

The reagents used in the experiments were of analytical grade.

Gelatin solution preparation and its coating on salmon

Gelatin (4 g) obtained from refiner discharge was added to deionized water and stirred for 30 min at 50°C until dissolved. Glycerol and sorbitol as plasticizers were added at 60% and 1%, respectively, based on the protein content, before stirring for another 10 min. The resultant film-forming solution was filtered under vacuum in a Buchner funnel with Whatman no. 3 filter paper (110 mm diameter) to remove any undissolved particles, and the clear filtrate was used as a solution for subsequent gelatin coating.

Each of four salmon fillets was cut into six equal pieces. Half of the samples were left uncoated as controls, and the other half were coated with the

gelatin solution via the following procedure. Salmon samples were immersed in the gelatin solution at 5°C for 30 sec, allowed to stand for 2 min, and then immersed again in the gelatin solution for another 30 sec. Salmon from the control group was left untreated. The coated salmon samples were dried at 25°C for 30 min in a forced cold-air blast dryer to form the edible coatings and then stored at 5°C for subsequent quality assessment. All sample treatments were carried out in a cold room (5±1°C). Chemical analyses were performed at 2-3 day intervals to determine the overall quality of the fish samples.

Moisture, relative moisture loss, and volatile basic nitrogen (VBN)

Moisture content was quantified by oven-drying at 105°C, according to the AOAC procedure (1995), and the relative moisture loss was calculated as follows:

$$\text{Relative moisture loss} = \frac{M_i - M_f}{M_i} \times 100,$$

where M_i and M_f are the moisture content of the salmon samples immediately before and during storage, respectively.

The concentration of VBN was determined by the method of Conway (Ministry of Social Welfare of Japan, 1960).

Peroxide value (POV) and fatty acid composition

Total lipid for analyzing POV and fatty acid composition was extracted with a chloroform/methanol mixture (2:1, v/v), according to the method of Bligh and Dyer (1959).

POV was determined according to the AOCS official method Cd 8-53 (1990). One gram of the extracted oil was put into a 250 mL Erlenmeyer flask, to which 25 mL of an acetic acid/chloroform mixture (3:2, v/v) was added. The sample solution was mixed, and 1 mL of saturated potassium iodide was added to the flask. The solution was allowed to stand for 5 min in the dark, with occasional shaking; then 75 mL of distilled water was mixed in before adding 0.5 mL of 1% starch solution. The mixed solution was titrated with 0.05 N sodium thiosulfate until the blue/purple color had just disappeared. POV was expressed as milliequivalent (meq) peroxide/kg oil.

The fatty acid composition of the extracted oil was analyzed after methylation (AOCS, 1990) using a GLC (Shimadzu GC 14A; Shimadzu Seisakusho, Co. Ltd., Kyoto, Japan) equipped with a Supelcowax-10 fused silica wall-coated open tubular column (30 m×0.32 mm I.d.; Supelco, Inc., Bellefonte, PA, USA). The injector and flame-ionization detector were held

at 250°C; the column was programmed to heat from 180°C (initial time 8 min) to 230°C at 3°C/min and the final time was set at 15 min. Helium was used as a carrier gas at the constant inlet pressure of 1.0 kg/cm² with a split ratio of 1:50. Fatty acids were identified by comparison with authentic standards (Sigma-Aldrich Co., St. Louis, MO, USA). The fatty acid compositions were calculated as a percentage relating the integrated area under the peak of each fatty acid to the total integrated area of all fatty acids present.

Browning index

Browning indices of the gelatin-coated and uncoated samples were determined according to the method of Hirano et al. (1987). Ten grams of sample was added to 20 mL of 66% ethanol and then homogenized prior to filtering. The browning index was defined as the absorbance of the filtrates measured at 430 nm.

Statistical analysis

All experiments used completely randomized block designs, and analyses were carried out in triplicate. Mean values with standard deviations are reported when appropriate. Statistical analyses were done using analysis of variance (ANOVA). Significant differences between the means were calculated using Systat Statistical and Graphical Software (version 7.5K; SPSS, Inc., Richmond, VA, USA) at $P < 0.05$ (Steel and Torrie, 1980).

Results and Discussion

Relative moisture loss

Relative moisture loss of refiner discharge gelatin-coated and uncoated salmon samples stored at 5°C is shown in Fig. 1. Moisture from the gelatin-coated salmon evaporated rapidly until day 9 of storage and then remained unchanged ($P > 0.05$). During cold storage, the time course of moisture loss was similar in both the gelatin-coated and uncoated salmon; however, relative percentage of moisture loss was less in the gelatin-coated salmon. Jeon et al. (2002) reported that the relative moisture loss in chitosan-coated cod fillet increased rapidly during the first few days of storage but decreased beginning at day 6 of storage. Pham and Willix (1984) reported that the desiccated surface layer that develops during cold storage produced a resistance to further mass transfer in the case of biological substances, thus bringing about a reduction in relative moisture loss in cod samples after a certain period of storage. Differences in the pattern of the relative moisture loss of coated

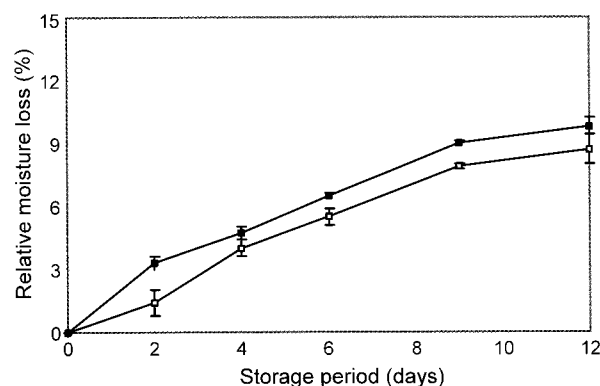


Fig. 1. Change in relative moisture loss of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated (□): gelatin-coated salmon, Uncoated (■): gelatin-uncoated salmon.

fish during cold storage among the reports of Jeon et al. (2002), Pham and Willix (1984), and the results reported here, are perhaps due to differences in the lipid content between cod and salmon.

The ability of edible films and coatings to act as a water vapor barrier is an important factor in their selection for use in several food systems. Stuchell and Kroeha (1995) reported on the efficient protection of salmon against water loss by using a coating composed of a mixture of whey protein and acetylated monoacylglycerols. Avena-Bustillos et al. (2006) reported that gelatin films obtained from cold-water fish were lower in water vapor permeability than those obtained from warm-water fish or mammals. They proposed that the low water-vapor permeability of gelatin films obtained from cold-water fish could be particularly useful for reducing the water loss from encapsulated drugs and refrigerated or frozen foods. Antoniewski et al. (2007) reported that a gelatin coating acts as a barrier to water and reduces the exudates that result from water loss in fresh meat products.

These results and these reports demonstrate the potential of using gelatin from Alaska pollock refiner discharge as a preservative coating to reduce or prevent moisture loss from salmon.

Volatile basic nitrogen content

The effect of gelatin coating on VBN content in salmon stored at 5°C is shown in Fig. 2. At the start of cold storage, the VBN content of the gelatin-coated samples was 14.3 mg/100 g, the same as that of uncoated samples. The VBN content of gelatin-coated salmon remained unchanged during the first few days of storage, but progressively increased

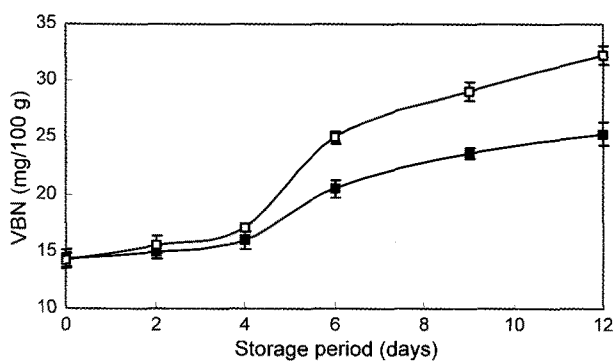


Fig. 2. Change in the volatile basic nitrogen (VBN) content of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated (-■-): gelatin-coated salmon, Uncoated (-□-): gelatin-uncoated salmon.

starting at day 4 of storage. The VBN content of gelatin-coated salmon increased by 1.8-fold compared to a 2.3-fold increase for the uncoated salmon after 12 days of storage, thus reflecting a 22% reduction in the formation of VBN in the gelatin-coated samples. During cold storage, the time course of change in VBN content was similar for both the gelatin-coated and the uncoated salmon; however, the gelatin-coated salmon showed reduced VBN formation throughout the entire storage period compared to the uncoated salmon. The limit of acceptability of VBN in fish, according to the Decision of the European Commission from March 8, 1995 (EU, 1995) (Castro et al., 2006) and other researchers (Baixas-Nogueras et al., 2001; Castro et al., 2006; Kim et al., 2002) is 25-35 mg/100 g of fish. This value was reached after 6 days of storage in the uncoated salmon versus 12 days in the gelatin-coated salmon. The increase in VBN levels in fish during cold storage may be attributable to several enzymatic processes: namely, the deamination of free amino acids, degradation of nucleotides, and the oxidation of amines, among others (Ozogul and Ozogul, 2000). Jeon et al. (2002) observed that the acceptable 25 mg VBN per 100 g of flesh was exceeded after 6 days and 8 days of storage, respectively, for uncoated cod and herring stored at 4°C, compared to 8 days and 10 days, respectively, for chitosan (14 cP)-coated cod and herring stored at 4°C.

Peroxide value, fatty acid composition, and (20:5n-3+22:6n-3)/16:0 ratio

The effect of gelatin coating on changes in the POV of salmon during cold storage (5°C) is shown in Fig. 3. At the start of cold storage, the POV, a measure of the extent of deterioration of fats and oils,

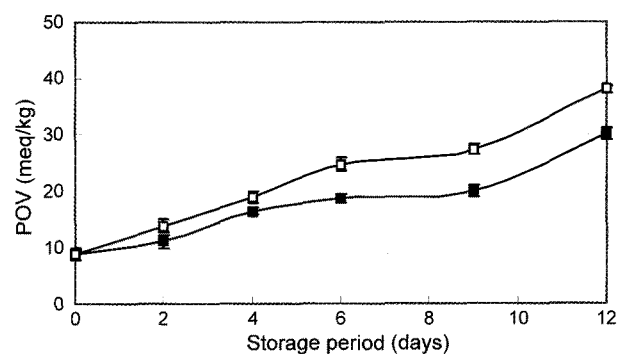


Fig. 3. Change in the peroxide value (POV) of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated (-■-): gelatin-coated salmon, Uncoated (-□-): gelatin-uncoated salmon.

of gelatin-coated and uncoated samples was 8.8 meq/kg and 8.9 meq/kg, respectively. The POV of gelatin-coated salmon slowly increased during the first few days of storage, then progressively increased beginning at day 9 of storage. On day 12 of storage, the POV of samples coated with gelatin was 21% lower than that of the uncoated salmon. The POV of gelatin-coated salmon was <20 meq/kg up to day 9 of storage, whereas the uncoated salmon exceeded this value on day 6 of storage. This protection by gelatin may be due to hydrogen bonding within the gelatin, making a good barrier to oxygen (Antoniewski et al., 2007; Krochta and De Mulder-Johnson, 1997). During cold storage, the time course of change in the POV was similar in both the gelatin-coated and uncoated salmon.

The effects of gelatin coating on changes in fatty acid composition and total lipid from salmon during cold storage (5°C) is shown in Table 1. The carbon number of fatty acids in all gelatin-coated and uncoated samples ranged from 14 to 22. Immediately at the start of cold storage, the percentages of saturated and monoenoic acids to total lipids were 26.3% (primarily 16:0, at 16.2%) and 29.3% (primarily 18:1n-9, at 14.8%), respectively, while the percentage of polyenoic acids was 44.6% (primarily DHA and EPA, at 14.9% and 9.5%, respectively). The percentage of saturated fatty acids to total lipids increased with increasing storage times for all the samples, whereas the percentages of monoenoic and polyenoic acids decreased. After 12 days of storage, the saturated fatty acid content showed an 8% increase in the gelatin-coated salmon, while the monoenoic and polyenoic fatty acid content showed a decrease of 6% and 12%, respectively. This increase in saturated fatty acids during cold storage was

Table 1. Change in the fatty acid composition of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C)

	(Area %)				
	0 day	6 days		12 days	
		Coated ¹⁾	Uncoated	Coated	Uncoated
14:0	5.9	6.7	6.7	7.2	8.7
16:0	16.2	16.9	17.3	18.2	19.6
17:0	0.5	0.4	0.4	0.5	0.6
18:0	3.7	3.5	4.0	4.0	4.4
Saturates	26.3	27.5	28.4	29.9	33.3
16:1n-7	7.1	7.9	6.9	8.0	8.4
17:1n-8	0.7	0.7	0.6	0.6	0.5
18:1n-9	14.8	14.2	14.6	13.5	12.8
18:1n-7	3.6	3.1	3.3	3.1	3.1
20:1n-9	1.9	1.9	1.8	1.8	1.6
22:1n-11	0.5	0.5	0.5	0.5	0.4
22:1n-9	0.2	0.2	0.2	0.2	0.2
24:1n-9	0.5	0.4	0.4	0.4	0.4
Monoenes	29.3	28.9	28.3	28.1	27.4
16:2n-4	0.9	1.0	1.0	0.9	1.0
16:4n-1	1.0	1.1	0.8	1.0	0.9
18:2n-6	6.9	6.8	6.3	6.1	5.7
18:2n-4	0.4	0.4	0.4	0.4	0.4
18:3n-4	0.5	0.5	0.5	0.5	0.5
18:3n-3	1.1	1.1	1.0	1.2	1.1
18:4n-3	1.3	1.3	1.2	1.3	1.1
18:4n-1	0.7	0.7	0.8	0.8	0.8
20:2n-6	0.4	0.4	0.5	0.4	0.4
20:4n-3	1.2	1.2	1.4	1.2	1.3
20:4n-6	0.9	0.9	0.8	0.9	1.0
20:5n-3	9.5	9.0	8.8	8.9	7.9
22:3n-6	0.5	0.5	0.5	0.5	0.4
22:4n-6	0.2	0.5	0.6	0.3	0.3
22:5n-3	3.9	3.6	4.3	3.8	4.1
22:5n-6	0.3	0.2	0.3	0.3	0.3
22:6n-3	14.9	14.3	14.0	13.4	12.2
Polyenes	44.6	43.5	43.2	41.9	39.4

¹⁾Coated: gelatin-coated salmon, Uncoated: gelatin-uncoated salmon.

primarily due to the percentage increase of 16:0. The relative percentage decrease in monoenoic and polyenoic acids, however, was attributable to decreases in 18:1n-9, DHA, and EPA (Jeong et al., 1995). Similar results were observed during the cold storage of fresh fish and its products (Ozden, 2005). During cold storage, the time course of the changes in fatty acid composition was similar for both gelatin-coated and uncoated salmon, but the extent of the changes was less in the gelatin-coated samples.

To illustrate more clearly the change in fatty acid composition during cold storage, the effect of gelatin coating on the (20:5n-3+22:6n-3)/16:0 ratio in salmon stored at 5°C is shown in Fig. 4. The (20:5n-3+22:6n-3)/16:0 ratio was 1.51 for salmon sampled

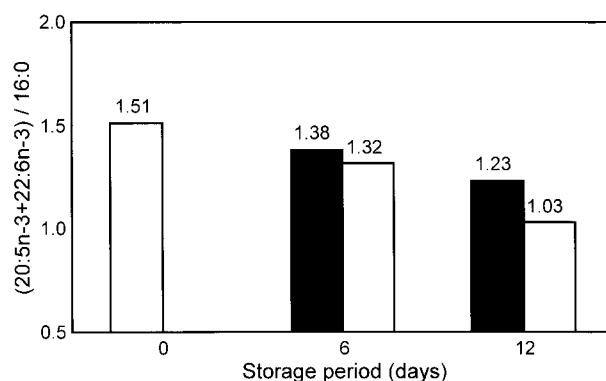


Fig. 4. Change in the (20:5n-3+22:6n-3)/16:0 of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated (■): gelatin-coated salmon, Uncoated (□): gelatin-uncoated salmon.

immediately at the start of cold storage, and this value decreased in both gelatin-coated and uncoated samples during cold storage. The (20:5n-3+22:6n-3)/16:0 ratio in gelatin-coated salmon on day 6 and day 12 of storage was 1.38 and 1.23, respectively; these values were 5% and 19% higher, respectively, than the ratios observed in the uncoated samples on the same days.

Browning index

The effects of gelatin coating on the browning index in salmon stored at 5°C is shown in Fig. 5. In salmon sampled immediately at the start of cold storage, the browning index of gelatin-coated and uncoated samples was 0.543 and 0.545, respectively. The browning index of gelatin-coated salmon progressively increased throughout the entire storage period. On day 12 of storage, the browning index of gelatin-coated salmon was 6% lower than that of the

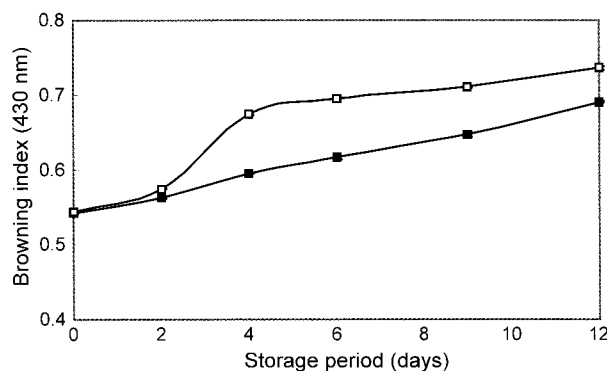


Fig. 5. Change in the browning index of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated (-■-): gelatin-coated salmon, Uncoated (-□-): gelatin-uncoated salmon.

uncoated salmon. During cold storage, the time course of change in the browning index was similar for both the gelatin-coated and uncoated salmons. In general, the browning reaction in foods is due to lipid oxidation, Maillard reaction, and caramel reaction (Hirano et al., 1987). From the results of POV and fatty acid composition measurements, the change in browning index that occurred in salmon during cold storage is attributable to lipid oxidation. Antoniewski et al. (2007), who studied the effect of gelatin coating on the shelf life of fresh meat, reported that gelatin-coated samples, such as whole beef tenderloins, whole pork loins, chicken breasts, and salmon, that display a smaller total color change than their uncoated counterparts, would have an extended shelf life. Keil et al. (1960) found that beef loins and sausage brushed with a solution of gelatin had a color that was visually equal to their respective colors prior to storage.

Sensory appearance

Photographs of refiner discharge gelatin-coated and uncoated salmons stored at 5°C are shown in Fig. 6. The gelatin-coated salmon sampled immediately at the start of cold storage looks like a product of higher grade because of its glistening polish, which was maintained up to day 12 of storage. When oxy-myoglobin is oxidized to metmyoglobin, consumers reject salmon products. In this sense, the color of salmon is very important. The color of both gelatin-coated and uncoated salmons changed as the storage period increased. During cold storage, the extent of sensory color change in the gelatin-coated salmon was less than that of the uncoated salmon. The gelatin coating on salmon probably reduced the color deterioration by acting as a barrier to oxygen (Antoniewski et al., 2007).

From the results of chemical measurements, such as the relative moisture content, VBN, POV, fatty acid composition and $(20:5n-3+22:6n-3)/16:0$ ratio, and sensory color change, the coating of salmon with refiner discharge gelatin effectively suppressed moisture loss, lipid oxidation, and color deterioration over the entire storage period.

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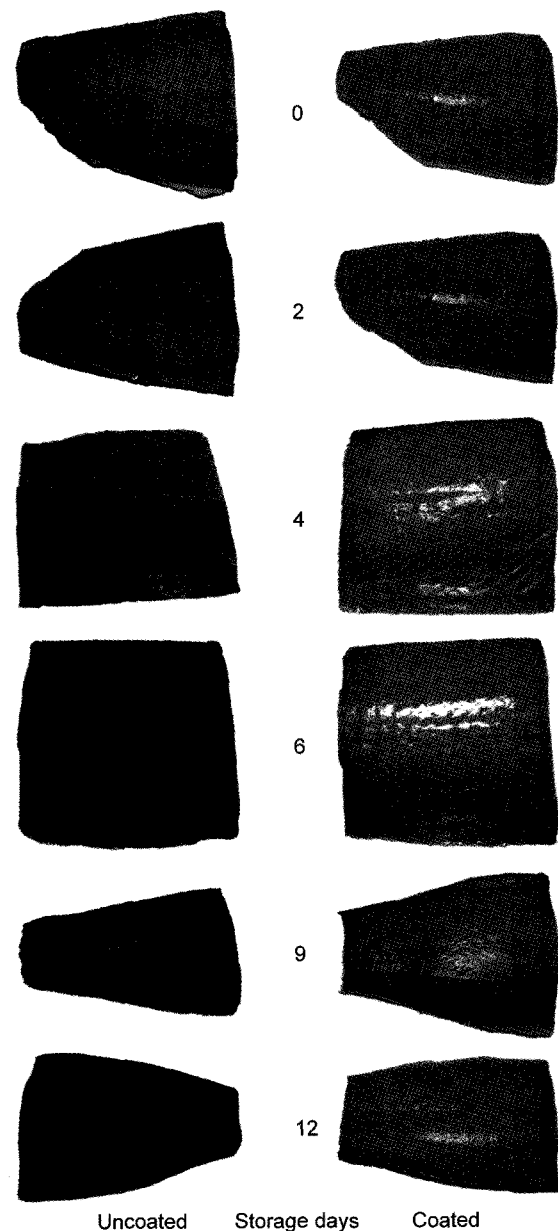


Fig. 6. Photographs of refiner discharge gelatin-coated and -uncoated salmons during cold storage (5°C). Coated: gelatin-coated salmon, Uncoated: gelatin-uncoated salmon.

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