Establishment of Japan Eco-Leather Criteria based on Type I Environmental Label

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Abstracts: The Japanese Association of Leather Technology (JALT) established the Japan Eco-Leather Criteria (JEC) newly referring to the procedure of ISO 14020 and 14024. The eco-leather was defined as leather that considered environmental impact reduction over the life cycle. A part of JEC was applied to Japan's Eco Mark certified leather goods, and the eco-leather came to be widely evaluated by the consumer. By waste-disposal time in Japan, it announces that the treatment of high temperature melting furnace is progressing, the leather incineration technique of 1100 degrees C or more prevent the formation of hexavalent chromium, and the slag is used effectively for concrete aggregate.
Key words: Eco-Leather; Eco Mark; environmental impact reduction; incineration; hexavalent chromium

1 Introduction

The approach of a certification product for Eco Mark by the Japan Environment Association (JEA) had started in 1989 focusing on mass consumption goods, such as stationery and uniform clothing [1]. This is because leather goods were diverse-types-and-small-quantity production, so there were not able to adapt themselves in such new environmental activity. However, an environmental practice and the environmental label come to be paid to attention with the rise of the high value-added production in a leather domestic and foreign market, and, at last, the chance of environment-related business has come to leather and leather goods [2-4]. Based on ISO14024, as requirement criteria of environmental impact items covering all life cycles, third-party certificate and the attached certificate were selected, and each standard value was decided upon at the JALT. In this announcement, it is described to examine the following four subjects, namely, the nonconformity to criteria of the forerunner testing agency, the decision of hazardous substances criteria, the fixation of this test method, and the investigation on reducing hexavalent chromium in the waste-disposal treatment, and it is described for these results to be applied to Japan's Eco Mark certified leather bags and shoes, and to have led to the expansion of the eco-leather.

2 Experimental

2.1 Materials

All of 212 pieces leather made in domestic and foreign from the Japanese market, were extracted at random from 2002 to 2008, and were analyzed. The foreign leather was from the following countries, Spain, France, Italy, Britain, China, Korea, India, Indonesia, Pakistan, Indonesia, Bangladesh, and Thai.

2.2 Selection of Environmental Impact Assessment

In order to decide upon the certificate requirements for environmental impact reduction, the environmental impact item was selected from a matrix of environmental criteria which followed ISO 14024 through the stakeholder's conference. In the environmental impact reduction at the disposal process, incinerating reactions were investigated to prevent the formation of hexavalent chromium.

2.3 Non-conformity investigation to the elution test of commercial leather

In the forerunner 4 following testing agencies, i.e., TESTEX, NISSENKEN, PFI-SG mark, and JILR (a

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JEC criterion is carried out), the non-conformity of commercial leather to each application criterion was investigated.

2.4 ***Decision of the environmental criteria and the test method***

The reduction to use and discharge of hazardous substances being made the most important among the selected environmental impact items, it decided upon the elution criteria of limit value and the test method.

3 Results and discussion

3.1 Selection of Environmental Impact Items and certificate requirements

In consideration of environmental impact reduction over the whole life cycle of a product, it was classified into two from the predominancy of the reduction as shown in Table 1. Among both, the mark (●) was selected by the certificate requirement and the mark (○) was not selected by the certificate requirement. The blank indicates items that were not considered, or the items to be considered with any other item.

At first use/discharge item of the hazardous substance(8) was selected from the objective achievement of environmental impact reduction being most expected at the time of manufacturing (B8), use consumption (D8),disposal (E8).

Next, among all the environmental impact items(1-9), in items(1,4,7) related to the by-product resource utilization of the animal skin, and items(2,3,5,6,7) related to observance of environmental laws, the environmental impact reduction in each whole life cycle is important, and was shown in Table 2 as the documentation of certificate requirements which can prove the objective achievement. The test certificate of the hazardous substance was also shown here simultaneously.

Tab. 1 Chart for Selecting Environmental Impact Items at Each Stage of product to the Eco-Leather

Environmental Impact Items	Product Life Stage					
	A Resource Extraction	B Manufac-turing	C Distribu-tion	D Use/Con-sumption	E Disposal	F Recycling
1. Resource consumption	●	●	●	●	●	
2. Discharge of greenhouse gases		○				
3. Discharge of ozone layer depleting sub.		●				
4. Destruction of eco systems	●					
5. Discharge of atmospheric pollutants		●				
6. Discharge of water pollutants		●				
7. Discharge/disposal of wastes	●	●			○	○
8. Use/disharge of hazardous substances		●		●	●	
9. Other environmental impacts		●				

In particular, in the time of disposal, in Japan, the operation of the high temperature melting furnace is progressing and the equation in a furnace is assumed as follows. That is, (1) formula is oxidation reaction in normal temperature [5], and the air, by (2) formula is a reduction reaction in 1400℃ or more [6], and it is shown that the generating of hexavalent chromium is prevented completely. As a result, trivalent chromium slag is solidified with silicate glass and detoxified. The opinion that this incineration technique can become certificate requirements of environmental impact reduction was offered.

$$2CaO + Cr_2O_3 + 1.5O_2 \rightarrow 2CaCrO_4 \quad (1)$$

$$CaCrO_4 + SiO_2 \rightarrow CaSiO_2 + 1/2Cr_2O_3 + 3/4O_2 \quad (2)$$

Tab. 2 Certificate requirements to the Eco-Leather

Certificate	Certification procedure	Matrix sign of Table 1
Hide and skin supply certificate	Supply (sale) place invoice	A1,A4,A7
Microscope leather section photograph	Document from third party organization	A1
Environmental-laws observance certificate	Declaration from tanner	B2,B3
Hazardous substance tested certificate	Document from third party organization	B8,D8,E8
Carcinogenic dyes non-used certificate	Certification from dye seller and tanner	B8,D8,E8
Leather handling information booklet	Document of concrete handling method from tanner	B1,C1,D1
Quality conformance certificate	Document from third party organization	D1,E1

According to our investigation of household waste in the prefectural capital in Japan, 83% of leather goods are incinerated [7]. In recycling (F7, F8) of the incineration ash, results are piled up with steady steps. For example, the final slag shows the acceptance criterion of 0.05mg/l or less in the elution of hexavalent chromium, and is being recycled by a lot of aggregate for concrete etc [8]. However, the certificate requirement was not selected for the reason on "the pursuit of a course which results in disposal in the present condition was difficult, and similarly, the recovery system of disposal leather was not completely established in recycling".

Furthermore, when leather was seen from the position at the time of resource extraction(A), it was judged that especially the predominancy of the environmental impact reduction in resource consumption(A1), the influence on an ecosystem(A4), and disposal of waste(A7) was high, and was adopted as certificate requirements. For the result, for example, as shown in certificate requirements of Table 2, the raw hide invoice from a packer, the split discharge invoice from a tanner, the prevention of animal species (kangaroo etc.) from the organization, serve as effective documents.

From the above result, it can be called an "eco-leather" with the leather "Provided with the certificate requirements which the reduction of environmental impact covering the whole life cycle is satisfied". In order to define leather, the microscope section photograph proving finish film thickness being below 0.15mm (150μm) becomes indispensable[9]. These, such as composite leather or leather board which kneaded the leather fiber and the synthetic resin, or synthetic or artificial leather etc., are excluded from certification.

3.2 Non-conformity investigation to the elution test of commercial leather

From the elution test result of hazardous substances, the Non-conforming appearance ratio to the limit value for various product classes was shown in Table 3. Here, the non-conforming appearance ratio is that the sample total which became non-conforming on the limit value for product class is divided by the sample total, and multiplies it in 100. In addition, the non-conforming appearance ratio applied and computed one low limit value for product class of each testing agency. It was total chromium, formaldehyde, lead, and cobalt order that an incompatible ratio was high in baby criteria. Among this four test item, the non-conforming ratio of total chromium in the baby limit value was as the highest as 56.7%. Usually, chromium in chrome-tanned-leather is a very stable trivalent state at the time of use of leather goods. However, by the

abnormal reaction at the time of manufacture, the conversion of trivalent chromium into hexavalent chromium is accepted [11], and hexavalent chromium may elute from leather at the time of analysis. As a result, as shown in Table 3, as for hexavalent chrome, 4.7% of a non-conforming ratio and the maximum of 68.0mg/kg were observed. The both criteria (see Table 4) of baby and adult, "below detection limit" are carrying out a very severe setup to prevent the elution of hexavalent chromium from the leather completely. The safety of consumers will be secured by the criteria.

Tab. 3 Non-conformity to the elution criteria for hazardous substances eluted from commercial leather

Product Class Non-conforming Regulated substances[*1,2]	Non-conforming appearance ratio,% to baby criteria	Non-conforming appearance ratio,% to adult criteria,%		Non-conforming Maximum mg/kg
		Direct contact[*3]	No direct contact[*4]	
Formaldehyde	36.2	12.4	7.4	268
Total Chromium	56.7	4.0		428
Lead	15.3	5.1		19.6
Cobalt	3.2	1.6		8.1
Hexavalent Chromium	4.7			68.0
Carcinogenic arylamines	8.0 (3.4)[*5]			346
Water extractable substances	2.5 (—)			5.3
pH value	6.4 (55.5)[*6]			3.1
Color Fastness to rubbing	5.9 (16.7)[*7]			—

[*1] Next carcinogenic amines were detected below detection limit, that is, they were five sorts of benzidine, 3,3-dichlorbenzidine, 4-aminobipheny, o-toluidine, 4-chloroaniline. [*,2] The following substance was not detected below detection limit That is, they were Tributyltin compounds, Pesticides, TeCP, Soluble mineral tanning agents (Al, Ti) ,and Other heavy metals (Antimony, Arsenic, Cadmium, Copper, Mercury, Nickel), [*3,4] with skin, [*5] <20mg/kg (<30mg/kg), [*6] pH3.5-7.0(pH4.0-7.5), [*7]with dry test, (wet test)

The non-conforming appearance of formaldehyde showed the 2nd high rate in the baby criteria of a hazardous substance. To this substance, it is regulated by the law from health risks, such as skin lesions, in other materials. Moreover, formaldehyde is used abundantly in the tanning process and is important as a test item.

The non-conforming appearance of lead showed the high rate that followed formaldehyde when comparing it by baby and adult's standards. Lead originates in red or yellow inorganic pigments, impurities of agents and shotgun marks etc. The baby criteria for lead (see Table 4) is very strict, there is a possibility of non-conformity in the use of small amounts of lead-containing pigments at the finish. A leaden baby criteria (refer to Table 4) may be very severe, and may become non-conforming also in little use. Therefore, it becomes important to certainly check the existence of lead content in leaden use at the time of chemical agents purchase.

The non-conforming ratio in the common criteria of baby and adult showed high rate in order of pH (4.0-7.5), the color fastness to wet rubbing, carcinogenic amine, pH (3.5-7.0), the color fastness to dry rubbing, hexavalent chromium, and water extractable substances. The highest ratio in these was 55.5% of pH (4.0-7.5). The pH criterion shows pH having extracted leather with water. The EU drinking water directive is in the

range of pH, pH6.5-8.5 and can be interpreted as a weak acid in the neutral area. It is understood in Table 3 that pH limit value made supposing the baby having sucked leather differs with testing agencies. It is very difficult for chrome tanned leather to pass > pH 4.0 criteria. Therefore, in the testing agency which has applied the criteria of this range, pH of the interior leather permits >pH3.5. That is, the appearance ratio is clear from decreasing sharply from 55.5% to 6.4% at >pH3.5. So, In this case, it was judged that explanation of the human body safety by pH standard was difficult for a consumer.

Next, azo dye which generates carcinogenic aromatic amines by a reduction reaction within a human body poses a problem. Azo dye has a high affinity with leather, and the history used abundantly is long. The appearance ratio of carcinogenic amine showed 3.4% on < 30mg/kg criteria, 8.0% by <20mg/kg criteria. Though it was natural, former one showed the high appearance ratio. Regulation of carcinogenic amine is defined by the law of each country, and, in this case, the former criterion was adopted.

The non-conforming appearance rate of color fastness shows 17% at the time of wet rub fastness shows 5.9% at the time of dry rub fastness. In the dark color nap leather at the time of wet rubbing, since the technical improvement is difficult, an understanding is needed in a consumption side. The following paragraph 3.3 describes the necessity for the item of the color fastness.

Water extractable substances mainly originate in soluble tannin and salts in leather. The appearance ratio and non-conforming maximum were comparatively low, and since most influences on a human body were not reported. It was not set as the object of a test item.

From the above result, formaldehyde, carcinogenic amine, hexavalent chromium, total chromium, lead, cobalt, and color fastness to rubbing, were selected as test items of the hazardous substance.

3.3 Decision of the environmental criteria and the test method

Hazardous substances criteria and the test method were decided upon like Table 4 based on the following three fundamental views. 1) Here, the hazardous substance at the time of tanning process regulated by the law in a lot of countries is taken up attaching importance. 2) Non-conforming appearance ratio and the maximum which described in Table 3 of preceding clause 3.2 that is test results of the forerunner environment label criteria are paid to attention. 3) It considers so that the healthy insecurity resulting from leather, for example, decoloring, bad smell, attached metal allergy, etc. may be canceled.

The criteria of hazardous substances have specified the quantity of hazardous substances which elute from leather.All test items should show below limit value so that the eco-leather is recognized.

Formaldehyde criterion shown in Table 4 originates in Japanese law given to textiles [12]. The non-conforming appearance ratio of formaldehyde to the criteria was high, and carcinogenicity was also high (it belongs to the group 1 of IARC) shown in Table 3, therefore there were few objections to adopting test items. However, the baby limit value of formaldehyde based on Japanese law is too severe for natural fibers, such as wool etc. [13], it also has the request of deregulation. To be sure, the subject remains about the migration from other materials around 16 mg/kg at the time of consumption and sale of leather goods.

Total chromium consists of trivalent chromium and hexavalent chromium. The hexavalent chromium has a strong oxidizing power at the acidity of the pH, especially among these substances, and it belongs to group 1"Carcinogenic to humans" in the evaluation of IARC. Therefore, considering the safety of consumers, the elution of the hexavalent chromium cannot be allowed from leather. By the EU-WEEE/RoHS/ELV Directive, although hexavalent chromium is regulating the content in leather, these are not regulated about trivalent chromium. Usually, since it was not assumed that chrome tanned leather receives an oxidization action powerfully at the time of consumption, 50mg of baby and the 200mg/kg adult that was a more realistic SG-PFI criteria were adopted.

Tab. 4 Criteria for hazardous substances and the test method to the Japan's Eco Leather

Parameters Regulated substances	Applications Criteria Value Baby// Adult 1/ Adult 2			Test Method	Regulation Basis
Formaldehyde	<16mg/kg//<75mg/kg/<300mg/kg			JISL1041, J.Law112	MHLW:Min.Ord.No.34
Total Chromium	<5.0 mg/kg//<200 mg/kg			IUC27-1,2	KrW-/AbfG ,SG-PFI[*5]
Cr(VI)	Not detectable//Not detectable (<3.0 g/kg)			IUC18,DIN53314	2000/53/EC
Lead	<0.2 mg/kg//<0.8 mg/kg			IUC27-1,2, DIN38406-6,22	2000/53/EC, EkoTex[*6]
Cadmium	<0.1mg/kg//<0.1 mg/kg			IUC27-1,2, DIN38406-19,22	2000/53/EC
Cobalt	<1.0 mg/kg//<4.0 mg/kg			IUC27-1,2, DIN38406-11,22	67/548/EEC
Nickel	<1.0 mg/kg//<4.0 mg/kg			IUC27-1,2, DIN38406-11,22	67/548/EEC, 94/27/EC
Mercury	<0.02mg/kg//<0.02mg/kg			IUC27-1,2, DIN38406-11,22	2000/53/EC
Pentachlorophenol	<0.05 mg/kg//<0.5 mg/kg			IUC25	35LMBG82-2-8
Cleavable arylamine	Not detectable// Not detectable(<20 mg/kg)			IUC20,ISO/TS1723	35LMBG82-2-3
Carcinogenic dyes	Not used //Not used			35LMBG82-02-3	Eko-Tex
Odour	>3grade// >3grade(no abnormal odour)			SNV195651	Eko-Tex, SG-PFI
Color Fastness [*1]	Finish [*4]1	Finish 2	Finish 3	ISO11640	—
Dry rubbing test [*2]	3-4//3-4	3-4//3-4	2-3//2-3	—	—
Wet rubbing test [*3]	2-3//2-3	2-3//2-3	2//2	—	—

[*1]1kg load for grain and 500g load for nap leather, [*2]1kg load,50strokes (Felt grade), [*3]1kgload,20strokes(Felt grade)

[*4] Finish 1; Pigment finish leather, Finish 2; dark shade and natural finish leather, Finish 3; pale shade and natural finish leather

[*5] SG-PFI; „SG-The label “, Prüf- und Forschungsinstitut Pirmasens e.V, [*6] Eko-Tex; Oeko-Tex Standard 100

Lead-containing pigments, also known as lead chromate (PbCrO4.PbO) still are used for leather finishing. It is known that inorganic lead has toxic effects on the peripheral nervous system also in a very small quantity [14]. Therefore, the very severe elution criterion is set up supposing baby swallowing the product of lead accidentally. In the present condition, since the change to lead free pigment in a tanning industry community was still considerably late, this standard was anxious for the change being rash, and adopted the baby limit value of Oeko-Tex 100 as 0.2mg/kg. However, there are also a lot of problems for the reasons of the difference in the extracting lead methods from leather, the height of demand detection sensitivity, etc.

Four heavy metals, Nickel, Cobalt, Mercury, and Cadmium, are the substances included in (3) of an above-mentioned fundamental view. It is considered that these metals work as impurities of old complex dye or chemical agents used, and make the criteria non-conforming. The metal actually observed as non-conforming as shown in Table 3 was only Cobalt. The onset of allergic contact dermatitis of leather and leather goods is based little on the heavy metal which eluted from leather, but rather the many of them originate in nickel, cobalt, cadmium mercury, etc. which eluted from metal belt like a wristwatch or metal attached to leather goods. The standard values of these metals were tuned to Oeko-Tex 100. Although non-conforming appearance for cadmium and mercury were not seen in Table 3 since four heavy metals of lead, mercury, cadmium, and hexavalent chromium were regulated by directives of EU-WEEE/RoHS/ELV described previously, sufficient cautions are required for the leather goods related to directives.

Carcinogenic aromatic amines were taken up for 22 kinds based on the German Food and Consumer Goods Law.

Although many new azo dyes are safe, in order to ask for relief certainly, it must be proved that the dye has not used cleavable arylamines as a composition ingredient. To prove the safety, the extracted artificial perspiration solutions are reduced compulsorily, and the generated cleavable arylamines are analyzed using a high sensitivity precision equipment. Here, the detection limit was set to <20mg/kg and the criteria value was adopted "not detected".

PCP is prohibition of manufacture from 1975 by the laws of Japan, as shown in the margin of Table 3. Other chlorinated organic compounds were not detected by commercial leather including PCP. Here, it gazed only to PCP that had been used abundantly at the tanning process among the chlorinated hydrocarbons. PCP is classified into 2B according to IARC, and has possibly carcinogenic to humans. Moreover, it poses a problem that PCP is related to the dioxin contamination from waste incineration and the impurities origin [15].

As mentioned above, on these criteria, it aligned with Oeko-Tex 100 or SG-PFI label, and the severe limit value was set up. The following two test items, that is, odour and Color Fastness to rubbing have the meaning in the correspondence to 3) of the fundamental view described before, and disclosing information that doesn't give leather distrust. Odour was tuned to Oeko-Tex 100 and the SG label, and the test method followed the Switzerland national standard SNV. Fastness to rubbing followed the standard of ISO or SG label.

As for the above result, among certificate requirements to eco-leather, main hazardous substances criteria were applied to the leather criteria of Japan's Eco Mark leather goods from August, 2007, and made the cause for eco-leather to be widely evaluated by the consumer.

4 Conclusions

The certificate requirements were established from selection of the predominance item of the environmental impact reduction in the whole for a life cycle of the leather. First, the elution test of market leather was done in forerunner testing agency, and seven sorts of formaldehyde, heavy metals, chlorinated organic compounds, dyes (carcinogenic aromatic amines and carcinogenic dyes), color fastness, odour and 14 kinds of details were chosen from non-conformity result of each test item as hazardous substances.

Furthermore, it tempered with the condition of baby and adult, and skin contact and a leather kind, and the limit value of 42 kinds of total was finally settled on. These Hazardous substances criteria were added, and the following seven other certificate requirements, that is, hide and skin supply certificate, microscope leather section photograph, carcinogenic dyes non-used certificate, environmental-laws observance certificate, leather handling information booklet, quality conformance certificate were decided and the eco-leather was authorized by passing of these environmental criteria.

Note: at present, the Japan Eco-Leather Criteria proposal of JALT is transferred to JLIA, advancing the schedule preparation for starting the certification business from this year.

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