No. 74

Japan Hygienic Association of Vinylidene Chloride Newsletter

April 2012 REVISED

Barrier functions of polyvinylidene chloride in food packaging applications

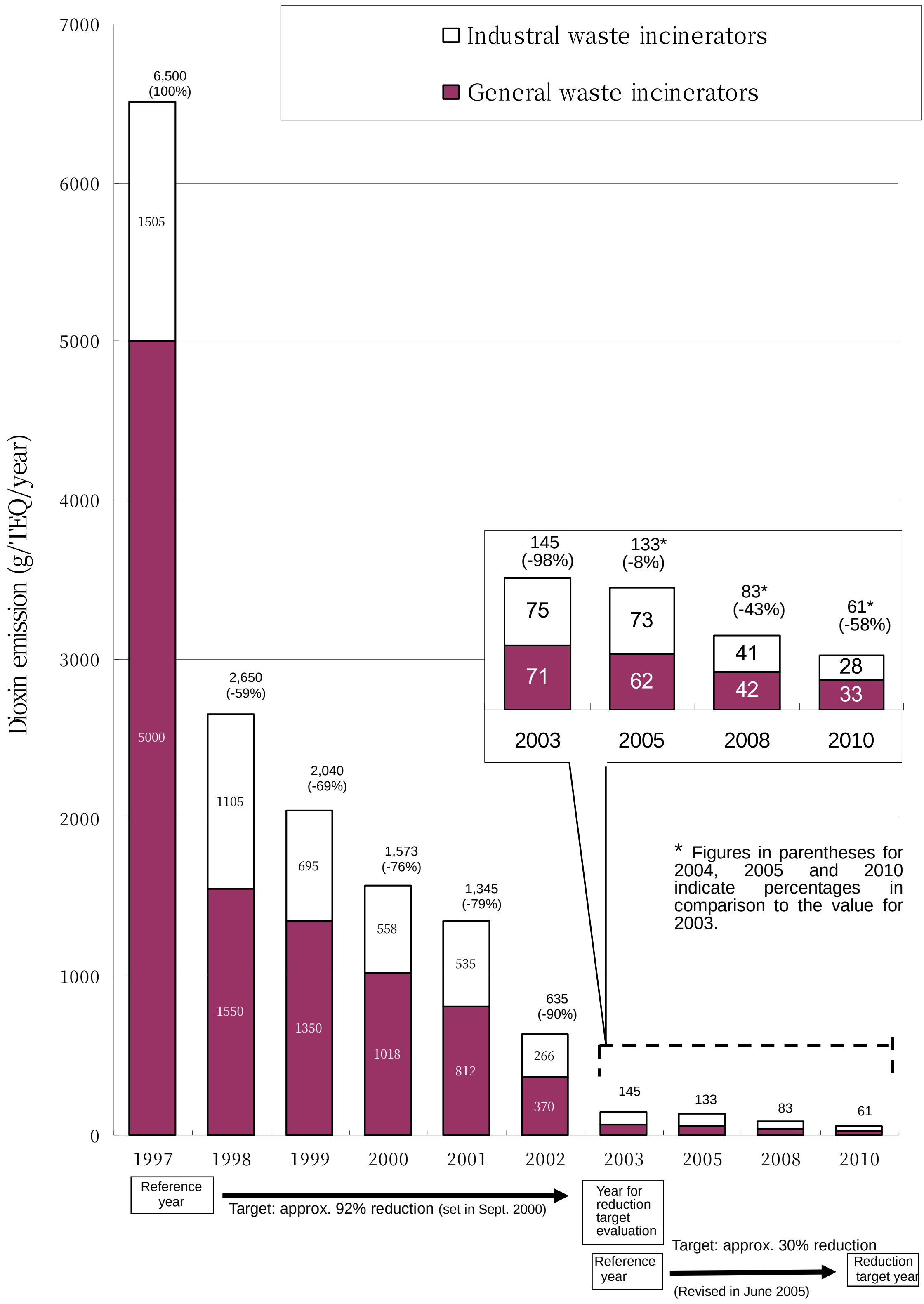
Japan Hygienic Association of Vinylidene Chloride
Coating materials and coating section meeting

1. Introduction

Polyvinylidene chloride-coated (PVDC-coated) films provide excellent oxygen gas barrier properties that are minimally affected by humidity, which makes them applicable in a variety of environments. Due to their excellent moisture-blocking properties, they have been widely used as packaging materials since around 1953[1). However, because of the dioxin problem that came to light in around 1997, the use of PVDC-coated films as packaging materials has declined. A number of film manufacturers have placed non-chlorine gas barrier films on the market, and these have increasingly replaced PVDC-coated films. To combat the problem of people's avoidance of PVDC-coated films, the Japan Hygienic Association of Vinylidene Chloride has made efforts to gain the confidence of users of vinylidene chloride resin, providing information in its newsletters and other reports on the relationship between the combustion of polyvinylidene chloride and dioxins[2)–4)] and on the environmental burdens of PVDC-coated films[5)].

Meanwhile, instead of restricting the use of chlorine plastic in order to reduce emissions of the dioxins in question, the Ministry of Health, Labour and Welfare set the goal of constructing a new type of incinerator capable of combustion at high temperatures (over 800˚C) and equipped with other measures for reducing these emissions. The resulting reduction in dioxin emissions has been greater than expected, as shown in Figure 1. Because of this, the market's misconceptions about PVDC-coated films have been mostly cleared up, and their value as barrier packaging materials has been rediscovered. Against such a background, this article reports on the results of comparisons of PVDC-coated films with other types of gas barrier films in regard to their roles as an oxygen barrier, a water vapor barrier, an aroma barrier and a material to extend shelf life. Such comparisons have been conducted before, but were repeated for the purpose of evaluating the usability of the different film types.

Fig.1: Changes in dioxin emissions from waste treatment plants
Source: Data published by the Ministry of the Environment on Mar. 2012



2. Evaluation of physical properties

The laminate films listed in Table 1 were used as samples for evaluation.

Table 1: Laminate films used for measurement

	Classification	Laminated structure
①	PVDC-coated films	K-OP (20 μm) // LLDPE (50 μm)
②		K-ONy (15 μm) // LLDPE (50 μm)
③	Non-chlorine films	MXD-ONy (15 μm) // LLDPE (50 μm)
④		VM (transparent)-PET (12 μm) // LLDPE (50 μm)
⑤		VM (transparent)-ONy (15 μm) // LLDPE (50 μm)
⑥		PVA-OP (20 μm) // LLDPE (50 μm)

Abbreviations:
K-OP: PVDC-coated biaxially oriented polypropylene
LLDPE: linear low-density polyethylene
K-ONy: PVDC-coated biaxially oriented nylon
MXD-ONy: nylon 6/MXD-6 bilayer biaxially oriented nylon
VM (transparent)-PET: transparent vapor-deposited biaxially oriented polyester
VM (transparent)-ONy: transparent vapor-deposited biaxially oriented nylon
PVA-OP: polyvinyl alcohol-coated biaxially oriented polypropylene
//: Dry laminate
Figures in parentheses indicate thickness.

2-1. Oxygen gas barrier properties

Experiment:
The oxygen transmission rate of each type of laminate film was measured in accordance with JIS K-7126B at 20˚C and at relative humidity values of 40%, 60%, 75% and 90%. Oxtran Model 2/20, manufactured by Modern Controls, Inc., was used as the test equipment. The resulting measurements are shown in Figures 2-1 and 2-2.

In addition, flex tests were performed with 100 bending cycles at 23˚C and 50% RH using a Gelbo flex tester to evaluate flex resistance in terms of oxygen gas properties for films 1 to 5 above. For these samples, the oxygen transmission rate was measured at 20˚C with 60% RH and at 20˚C with 90% RH. The resulting oxygen permeability measurements, together with those taken before the Gelbo flex testing, are shown in Figures 3-1 and 3-2.

Fig.2-1: Humidity dependence of the oxygen transmission rate for each type of barrier film

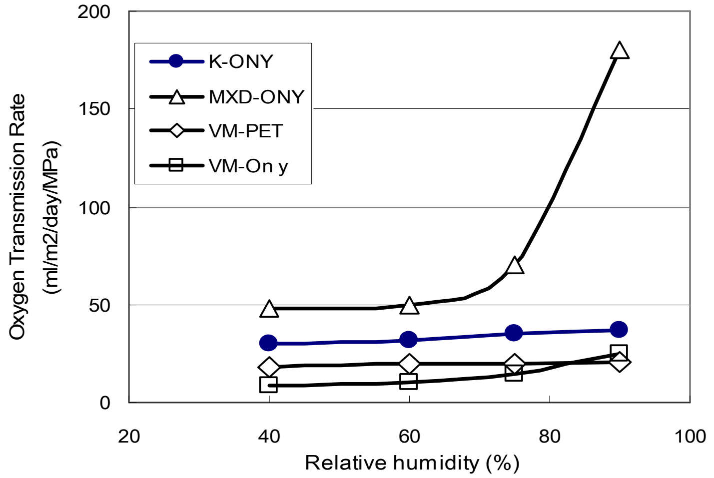
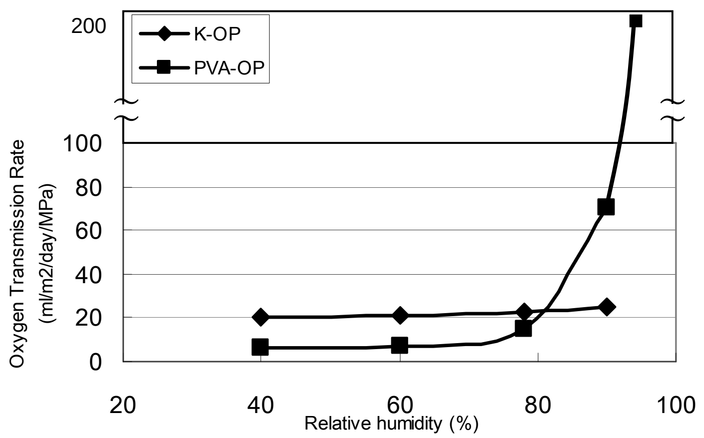


Fig.2-2: Humidity dependence of the oxygen transmission rate for each type of barrier film



As shown in Figures 2-1 and 2-2, the oxygen transmission rates of PVDC-coated films (K-OP and K-ONy) and VM (transparent)-PET were almost constant regardless of relative humidity. The oxygen transmission rates of MXD-ONy and PVA-OP, by contrast, tended to increase rapidly in a relative humidity range of 80% to 90%. As the oxygen transmission rate of PVA-OP at 20˚C and 90% RH exceeded 200 ml/m^2/day/MPa, it was impossible to reflect the data in the figure. It is assumed that this is because the barrier resin of PVA and MXD6 has a hydrophilic group, and that as a result, oxygen permeability increases due to water vapor in conditions of high relative humidity.

Figures 2-1 and 2-2 indicate that VM (transparent)-PET was superior to K-OP and K-ONy in oxygen permeability at 20˚C with a relative humidity of 90% or less.

However, it can be seen from Figures 3-1 and 3-2 that the oxygen permeability of VM (transparent) -PET significantly increased after the Gelbo flex testing. VM (transparent)-ONy, which has a vapor-deposited layer similar to that of VM (transparent)-PET, also showed a significant increase in oxygen permeability in the Gelbo flex test.

Fig.3-1: Gelbo flex resistance in terms of the oxygen transmission rate of each type of barrier film

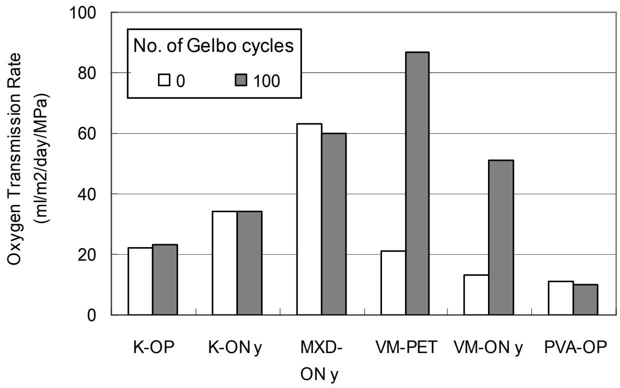
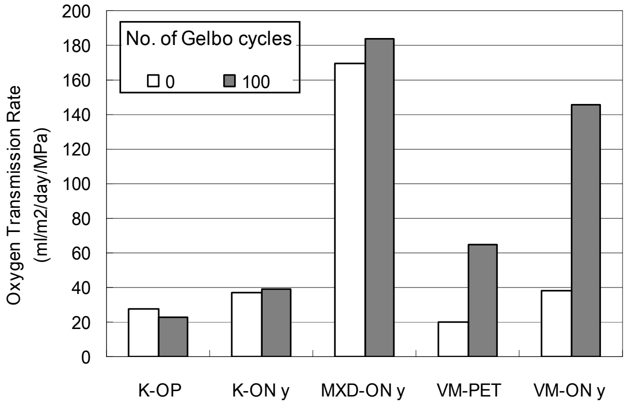


Fig.3-2: Gelbo flex resistance in terms of the oxygen transmission rate of each type of barrier film



The tough polymer known as PVDC is responsible for the gas barrier properties of K-OP and K-ONy, which means that these films are very high in flex resistance. By contrast, a vapor-deposited layer of metal oxide, which is low in flex resistance, is responsible for the oxygen gas barrier properties of VM (transparent)-PET and VM (transparent)-ONy, and as a result, the gas barrier layer was seemingly destroyed in the course of the test. Such flex resistance is an important quality in packaging materials during processing (printing and laminating) and transportation (after food has been packed). In this sense, it can be said that PVDC-coated films are excellent packaging materials.

As stated above, PVDC-coated films provide gas barrier properties unaffected by relative humidity, and are widely applicable in terms of package content and external environments. In addition, because of their high flex resistance, PVDC-coated films are known as packaging materials that maintain their oxygen gas barrier properties even when processed and transported as packages, and are considered safe to use.

2-2. Water vapor barrier properties

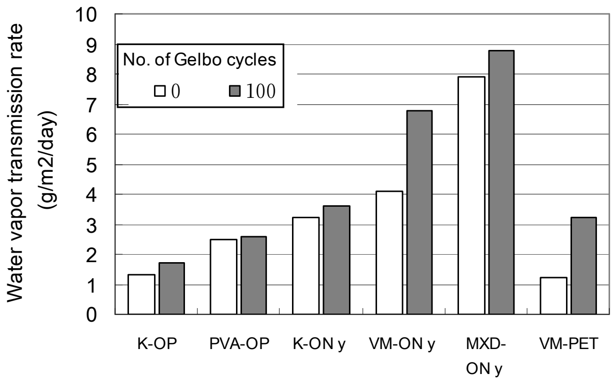
Experiment

The water vapor transmission rate of each laminate film sample was measured at 40˚C with a relative humidity of 90% in accordance with JIS-K-7129, using Permatran-W Model 3/33, manufactured by Modern Controls, Inc. In addition, Gelbo flex tests were performed in which films 1 through 6 in Table 1 each underwent 100 cycles of bending at 23˚C and 50% RH before the water vapor transmission rate was measured at 40˚C and a relative humidity of 90% or less. The results are shown in Figure 4.

Results and discussion

In the Gelbo flex tests, it was found that VM (transparent)-PET and VM (transparent)-ONy increased in water vapor permeability, just as they had in terms of the oxygen transmission rate. No increase in water vapor permeability was seen in the gas barrier films made with a tough polymer. K-OP and K-ONy in particular demonstrated lower water vapor permeability than other gas barrier films. The water vapor transmission rate of K-ONy after the Gelbo flex tests was approximately half that of the other nylon-based films, MXD-ONy and VM (transparent)-ONy.

Fig.4: Gelbo flex resistance in terms of the water vapor transmission rate of each type of barrier film



In the light of the widespread use of nylon-based films for the packaging of liquids, the use of K-ONy would result in a smaller loss of moisture content (weight) in packaged food products than the use of other nylon-based barrier films. This is a great advantage for K-ONy, as change in the weight of food products is an important quality control parameter.

3. Food storage

3-1. Testing of aroma barrier properties

Experiment

Three side-sealed bags measuring 70 mm × 70 mm were made from each sample film, and each was filled with 9 mL of vinegar. Each of the vinegar-filled packages was put in a brown wide-mouth reagent bottle with an airtight stopper. The bottles were sealed and stored in an environment maintained at 23˚C and 50% RH. After certain periods of storage, the aroma volatilized from each package within its bottle was evaluated by five panel members, and the average evaluation scores were regarded as the evaluation results. The evaluations were made on a scale of 1 to 5, with 1 representing no aroma and 5 representing an obvious aroma leak.

Results and discussion

The evaluation results are shown in Table 2. K-OP and K-ONy leaked no vinegar aroma even after one month of storage – a positive result in comparison to those of the other gas barrier films. Excellent aroma barrier properties can be seen as a valuable feature of PVDC-coated films, as many food products contain vinegar, such as delicacies, sauces, mayonnaise, *konbu* seaweed and red pickled ginger.

Table 2: Results of tests on the aroma barrier properties of each packaging material
Content: vinegar

No. of days	K-OP	K-ONy	MXD-ONy	VM (transparent)-PET	VM (transparent)-ONy	PVA-OP
1	1	11	1	1	1	1
2	1	1	1	1	2	1
7	1	1	1	1	1	3
14	1	1	1	1	4	4
21	1	1	1	1	5	5
28	1	1	1	2	5	5

Evaluation scoring: No aroma leak: 1 → 3 → 5: Aroma leak

3-2. Soy sauce color-change testing

Experiment

Color-change tests were performed on soy sauce using nylon-based gas barrier films (films 2, 3 and 5 in Table 1) and VM (transparent)-PET (film 4 in Table 1). As a standard sample, ONy (15)//LLDPE (50) was used in the tests. Three side-sealed bags measuring 70 mm × 70 mm were made from each sample film, and each was filled with 10 mL of soy sauce. After having been subjected to treatment process A or B, each soy sauce-filled package was stored in an environment maintained at 40˚C and 90% RH for a month, and OD values were measured after appropriate periods of storage.
Higher OD values indicate darker soy sauce color.
OD values were calculated using the following equation:

$$\mathbf{OD = Y_1 + Y_2 + Y_3 + Y_4 \qquad Yn = log_{10} l/(Xn \times l/100),}$$

where Y_1〜Y_4 are light transmission rates for 470, 500, 570 and 640 nm, respectively.
Process A: no treatment
Process B: soy sauce-filled packages placed in a revolving hexagonal-drum test machine lined with cardboard and rotated at 8 rpm for two hours

Results and discussion

The measurement results are shown in Figures 5-1 and 5-2. It was found that the longer the storage period, the larger the OD values were for each film sample. Figure 6 shows OD values both for samples that did and for those that did not receive treatment in a revolving hexagonal-drum test machine after 28 days of storage, together with the corresponding values before storage (initial values). The results shown in Figure 6 show the differences in OD values between the treated and untreated samples.

As shown in this figure, the relative color change of the soy sauce after 28 days was Ny > MXD-ONy > K-ONy > VM (transparent)-ONy > VM (transparent)-PET when hexagonal-drum treatment was not performed, and Ny > MXD-ONy > VM (transparent)-ONy > K-ONy > VM (transparent)-PET when such treatment was performed. Thus, the change in the color of the soy sauce for K-ONy was smaller than that for VM (transparent)-ONy when treatment was conducted. In addition, the figure shows that the differences in the change of OD values between samples that did and those that did not receive hexagonal-drum treatment were smaller for K-ONy than those for the inorganic vapor-deposited films (i.e., VM (transparent)-ONy and VM (transparent)-PET), just as the change in barrier properties (oxygen transmission rate and water vapor transmission rate) was smaller for K-ONy than for these other two.

This means that changes in the film properties of K-ONy due to shock during transportation and other processes after packaging are smaller than those for VM (transparent)-ONy and VM (transparent)-PET. Under the hexagonal-drum test conditions of this study, VM (transparent)-PET showed the most favorable results. However, based on differences in OD value changes between samples that did and those that did not receive hexagonal -drum treatment, and the trend toward degraded barrier properties after the Gelbo flex testing, K-ONy is considered to be the best among the samples evaluated in this study in terms of stability (taking into account the size of the bags actually used and transportation conditions).

4. Conclusion

As previously mentioned, PVDC -coated films provide stable properties of oxygen gas permeability in any conditions of humidity, and show only small changes in oxygen gas and water vapor transmission rates after being flexed. Accordingly, they can be considered suitable for a wide range of applications.

Market misconceptions about PVDC -coated films are now being cleared up, and a shift toward wider use in addition to their conventional appli -cations is being seen. PVDC-coated films are also being considered more as packaging materials for new food products, such as rice biscuits and pickles, that food manufacturers plan to put on the market. It is hoped that the overall performance of PVDC -coated films will be objectively evaluated, and that demand for them will grow.

Fig.5-1: Changes in OD values (without hexagonal -drum treatment) with storage time (no. of days)

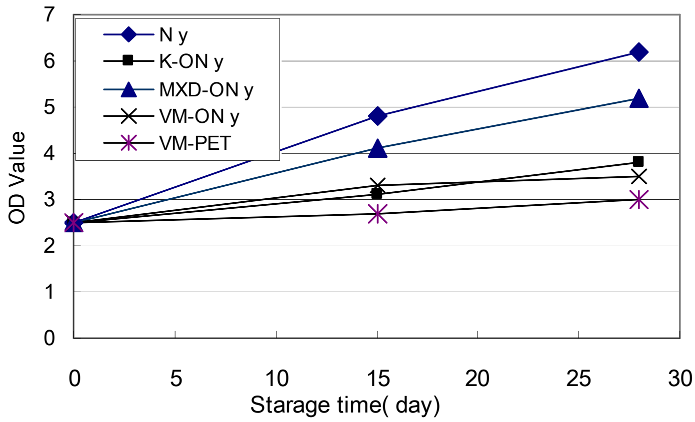


Fig.5-2: Changes in OD values (with hexagonal -drum treatment) with storage time (no. of days)

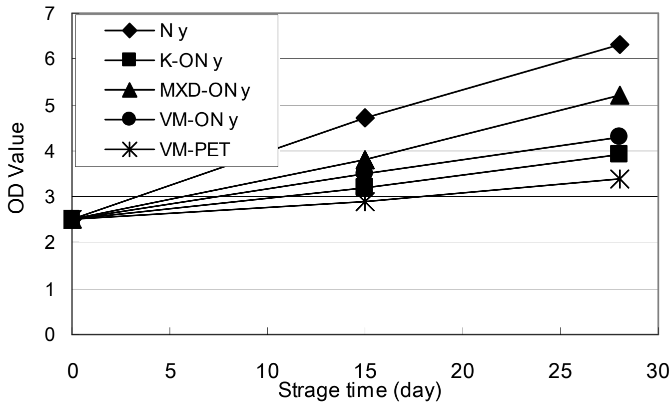
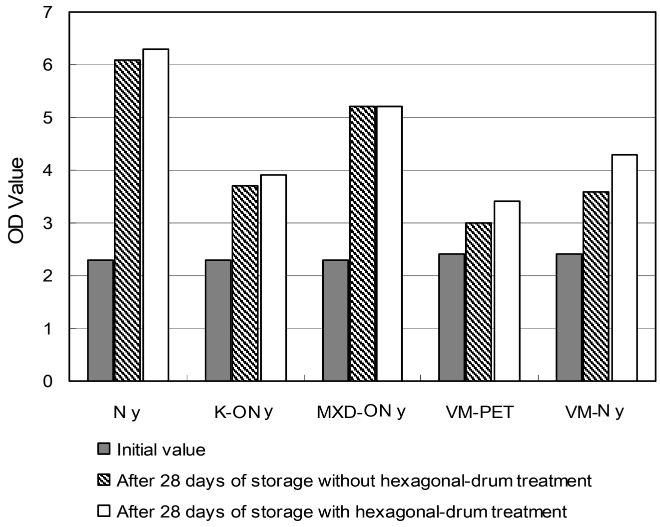


Fig.6: Results of testing (with and without hexagonal -drum treatment) on change in color of soy sauce



5. References:

1) Monthly Food Packaging Magazine. 1, 120 – 126 (2006)
2) Chemosphere. 44, 1389 – 1394 (2001)
3) Chemosphere. 54, 1521 – 1531 (2004)
4) Japan Hygienic Association of Vinylidene Chloride Newsletter. 63, 1 – 5 (2000)
5) Japan Hygienic Association of Vinylidene Chloride Newsletter. 62, 1 – 7 (2000)