乾性油の促進黄変試験

竹下寿雄・宮内徳之

(受理 昭和40年5月4日)

AN ACCELERATED TEST OF THE YELLOWING OF DRYING OILS

Toshio TAKESHITA, Noriyuki MIYAUCHI

An accelerated test using filter paper for the determination of the yellowing of drying oils is described. The method is as follows: 50 mg of sample are placed drop by drop in the center of a 40×40 mm square of Toyo No. 3 filter paper, then the unit is placed in a desiccator filled nitrogen for about 1 hr. for the purpose of diffusing the sample over the surface of the paper. The filter paper film is then placed in a desiccater containing NaCl saturated aq. solution. The desiccator is put in an forced draft oven keeped at 50°C or 75°C, and the amount of yellowing is determined by the difference in the absorbance measurements at 440 mμ and 720 mμ, using a clean white filter paper as reference standard, which is measured once a day for 5 days (75°C) or 10 days (50°C) in a Hitachi Model EPU-2 spectrophotometer, equipped with a reflectance accesory. Results of the tests on a number of common drying oils showed good agreement with the obserbed yellowing.

Introduction

Many studies done pastly about the measuring of yellowing property of drying oils. These most procedure used paints which prepared from the drying oils and pigments e. g. TiO_2. The paints coated on metal plates and the coated plates were suffered for the influence of heat and humidity. Then yellowness were measured from the reflectance spectrum of visible ray. But the calculation of yellowness from the spectrum is very troublesome. Then an accelerated test using filter paper for the determination of the yellowing of drying oils is described. Privett et al[1] proposed the method, but they did not controlled humidity which supposed to have large influence for the phenomenon.

Materials

Linseed oil, soybean oil, chineses tung oil, soybean oil fatty acid and dehydrated castor oil fatty acid were obtained from commercial souces.

Polymerized chinese tung oil was prepared by polymerization of chinese tung oil at 200°C for 1.5 hours, the polymerized oil had an iodine value of 82.9 and refluctive index of 1.5005. Dehydrated castor oil was prepared by esterification of dehydrated castor oil fatty acid with glycerol, which has iodine value of 152. 1, acid value of 5.7 and refluctive index of 1.4850. Urethane oil was synthesized by the reaction of soybean oil fatty acid di-ester of pentaerythritol with tolylen di-isocyanate.

Procedure

Preparation of film: A 40×40 mm square of Toyo No. 3 filter paper is placed on a small wire support on the pan of an analytical balance and weighed. Then about 100 mg of sample are placed drop by drop in the center of the paper. The samples are 50 %

xylene solution of above mentioned drying oils, and which containes Pb 0.4 % and Co 0.05 % dryer for the oil in the forms of naphthenate. So net 50 mg of the oil are placed on the paper. Then the unit is placed in a desiccator filled nitrogen for about 1 hr. for the purpose of diffusing the sample over the surface of the paper. This size of the paper is convenient to the spectrophotometer, and the reason of the using of 50 % solution of the oil is that the diffusion of the oil over the surface of the paper is not suffiicently if which placed on the form of oil only.

The filter paper film is then placed in a desiccator containing NaCl saturated aq. solution. The desiccator is put in an forced draft oven keeped at 50°C or 75°C, and the amount of yellowing is determined by the following method. The yellowing of the filter paper film was accelerated at the condition. Humidity was maintained at about75 % on the above each cases.

Measurement of yellowing: The amount of yellowing is determined by the difference in the absorbance measurements of reflectance (expressed as Δ optical density) at some two different wave lengths, using a clean white filter paper as reference standard, which is measured once a day for 5 days (75°C) or 10 days (50°C) in a Hitachi Model EPU-2 spectrophotometer, equipped with a reflectance accesory.

To determine the most appropriate two wave lengths for the above purpose, we measured the absorbance at 400mμ, 440mμ, 480mμ, 520mμ and 720μ, these measurements were done for 5 days (75°C) and 10 days (50°C) for 5 samples which is shown later. Then Δ optical density was calculated as follows:

Δ optical density (400–720)

= optical density (400mμ) − optical density (720mμ)

Δ optical density (400–720), (440–720), (480–720), (520–720) were then calculated. Δ optical density (400–720) changes of each samples at 75°C and 50°C were plotted against time respectively. Then Δ optical density (440–720), (480–720), and (520–720) were plotted similarly, the change of Δ optical density (440–720) at 75°C is shown on Fig. 1. The sample number of Fig. 1 is as follows: No. 1 linseed oil, No. 2 soybean oil, No. 3 dehydrated castor oil, No. 4 polymelized chinese tung oil, No. 5 urethane oil.

The yellowing order was given for each samples at each lapse of day from the results of above figures, of course the sample which had most large Δ optical density was ordered to first. Then these order from each figures were compared to the obserbed yellowing order. Then it was found that the order from the figure of Δ optical density (440–720) showed most agreement to the obserbed yellowing order. The two orders at the case of 75°C are shown on Table 1. The disagreement of the two order of Table 1 is mainly owing to the difficulty of judgment of observing yellowing order.

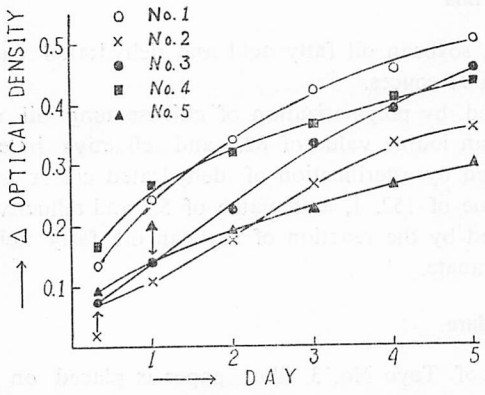

Fig. 1. Change of Δ optical density (440—720)

Table 1. Yellowing order of each samples (75°C)

Lapse of time (days)	Obserbed order	Order from Δoptical density (440–720)
8 hrs.	4 1 5 3 2*	4 1 5 3 2
1	1 4 3 5 2	4 1 3 5 2
2	1 4 3 5 2	1 4 3 5 2
3	1 3 4 5 2	1 4 3 2 5
5	1 3 4 2 5	1 3 4 2 5

* Sample number is same to Fig. 1.

Same results were obtained on the case of 50°C, then we named Δ optical density (440 –720) as Yellowing degree, and used to following study.

Results and Discussion

Influence of the quantity of the sample placed on the filter paper: 100g, 140g and 200g of xylene 50 % solution of linseed oil (+dryer) were weighed on the filter papers, then these pieces were tested for yellowing at 75°C and 50°C. Yellowing degree of the case of 100g sample was 0.33, 140g sample was 0.36 and 200g sample was 0.39 after 2 days at 75°C, and that of 100g was 0.51, 140g was 0.53 and 200g was 0.55 after 5 days at same temperature. About equal results were obtained at the case of 50°C. So we found that the quantity of the sample had some influence to yellowing degree in this method, but that was not so much,

Influence of temperature: 100g linseed oil solution test was done at 75°C and 50°C, and yellowing degree was compared. After 2 days the degree at 75°C was 0.33, however that of 50°C was 0.095, then after 5 days that of 75°C was 0.51, and that of 50°C was 0.20 respectively. Then 100g polymerized chinese tung oil test was done also at 75°C and 50°C. After 2 days that of 75°C was 0.32, that of 50°C was 0.08, after 5 days that of 75°C was 0.44, that of 50°C was 0.12. So we found that the temperature effect for yellowing was markedly.

Humidity effect: 100g linseed oil test was made not in desiccator at 75°C, other conditions were equally controlled, and this result was compared to above mentioned 100g 75°C test (75 % humidity). After 2 days the yellowing degree on this case was 0.21, after 5 days that was 0.30. The data was considerably small compared to the data of above 75 % humidity. Humidity on the case of no desiccator was lower doubtlessly. So it was found that humidity had much effect on the yellowing of drying oil films.

Dryer effect: 100g linseed oil test (not contain dryer) was done at 50°C. The yellowing degree on this case was 0.02 after 2 days, 0.09 after 5 days and 0.26 after 10 days. On the other hand the ordinary 100g linseed oil test at 50°C showed the degree of 0.095 after 2 days, 0.20 after 5 days and 0.28 after 10 days. So we found that dryer had much accelerating effect on the initial stage of the yellowing, but after many days this effect weakened, then yellowing degree on the case of no dryer overtook to that of ordinary dryer containing case.

Yellowing degree of some drying oils: The tests were made for linseed oil (No. 1), soybean oil (No. 2), dehydrated castor oil (No. 3), polymerized chinese tung oil (No. 4) and urethane oil (No. 5) which above mentioned at 75°C. After 2 days, the yellowing degrees are as follows: No. 1 0.34, No. 2 0.18, No. 3 0.22, No. 4 0.32, No. 5 0.19, and after 5 days No. 1 0.51, No. 2 0.36, No. 3 0.46, No. 4 0.44, No. 5 0.30 respectively. These order of yellowing degree was listed on Table 1 already. It was found that urethane oil yellowed initially, but its progress was comparatively slow, then after 5 days the degree of soybean oil surpassed to that of urethane oil. The yellowing order after 5 days are as follows: linseed oil, dehydrated castor oil, polymerized chinese tung oil, soybean oil, urethane oil.

Literature cited

1) Privett et al.: *J. Am. Oil Chemists' Soc.*, **38**, 22 (1961).
2) T. TAKESHITA et al., *Shikizai-kyokaishi (Japan)*, **37**, 381 (1964).