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IAFMM

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Our ref. 1991/31/S   Your ref.   Date 27th March 1991

TO: ALL MEMBERS OF THE SCIENTIFIC COMMITTEE

Dear Sirs

Re: Survey on fish meal stability and comparison of antioxidants by means of tests in an oxygen bomb

I have pleasure in enclosing a paper prepared by Mr Javier Zaldivar of Chile on the above subject. This will be discussed during the Scientific Committee meeting under agenda item 4.1.

Yours faithfully
International Association of Fish Meal Manufacturers

S M Barlow
Director-General

RESEARCH REPORT

1991-5

SURVEY ON FISH MEAL STABILITY AND COMPARISON OF ANTIOXIDANTS BY MEANS OF TESTS IN AN OXYGEN BOMB

SUMMARY

This survey studied fish meal stability to oxidation using the oxygen bomb method. A comparison was made of the stability of fish meal to which pure etoxiquin, and a mixture of etoxiquin, BHT (Butil hydroxitoluen) and lecithin had been added as antioxidants.

A method to improve the oxygen bomb method was sought, by determining the equipment's optimum operating conditions, as well as by establishing alternative stability criteria.

The findings indicate that using this procedure to determine fish meal stability is feasible. The use of a mixture of etoxiquin, BHT and lecithin seams to be less effective as an antioxidant than pure etoxiquin.

The survey was carried out in the laboratories of the Catholic University of Valparaiso by professors Samuel Navarrete and Patricio Proust, under the supervision of Javier Zaldivar.

INTRODUCTION

In the final stage of the fish meal manufacturing process an antioxidant is added to avoid possible self-combustion of the product during storage and transport caused by various exothermal oxidation reactions which occur in fish meal.

One of the most commonly used antioxidants is etoxiquin, which is added in quantities of about 1000 p.p.m. Etoxiquin content should not fall below 100 p.p.m. at the moment of shipment according to the norms adopted by IMCO in 1973.

The use of a mixture of etoxiquin, BHT and lecithin has been proposed recently, which is assumed to have synergistic effects as antioxidant, and would be cheaper than pure etoxiquin.

The use of the oxygen bomb method, used for determining the stability of liquid fuels (ASTM D-525-55 AND D-873-65 norms), has been suggested as an alternative procedure for fish meals. This procedure has already been adopted in Peru. The method consists in measuring the reduction of the pressure of oxygen loaded together with a fish meal sample in a thermostatized reactor. It has been empirically established that fish meal is stabilized if the fall in pressure is less than 10 psi/hour.

Based on this data, this study has the following purposes:

- Comparison by means of the oxygen bomb method of fish meal stability in which pure etoxiquin (Standard AOX), and a mixture of 33% etoxiquin and 67% BHT and lecithin (Super AOX), have been used as antioxidants.

- Optimization of tests in the oxygen bomb, seeking for the best conditions to reduce the duration of the test. The fish meal's self-combustion temperature was determined previously as a safety measure.

- Determination of alternative stability criteria for the oxygen bomb method.

MATERIALS AND METHODS

The tests were performed with fish meal samples from different sources, ages and agglomeration degrees, which had been added either Standard AOX or Super AOX as antioxidants.

The oxygen bomb is a 500 mL capacity stainless steel reactor with thick walls, which is located in a themostatized propylene glycol bath. The reactor is connected to an oxygen pressure recorder which has been loaded together with approximately 60 grams of fish meal. The initial oxygen pressure is about 60 psig, and the temperature of the bath is kept constant at values that range between 100 and 120 C°. The duration of the test is approximately 3 hours.

Determination of the fish meal self-combustion temperature in pure oxygen was carried out in a 600 mL Parr reactor, which has agitation, temperature control and measurement and pressure measurement. The reactor was loaded with 4 grams of fish meal and oxygen at initial pressures of between 60 and 80 psig. The reactor's temperature was gradually raised until a sharp increase in pressure was recorded indicating the beginning of self-combustion.

Additionally, the residual etoxiquin contents was determined for some fish meal samples by means of the normalized method of the Instituto de Fomento Pesquero de Chile.

FINDINGS

1. Comparison of Antioxidants

1.1. Residual etoxiquin contents

Determination was made of the quantity of etoxiquin present in fish meal samples of different ages and state of pulverization and pelletization, which contained either Standard AOX or Super AOX.

The results of these determinations are shown in Fig. 1.

1.2. Tests in the oxygen bomb

Measurements were made in fish meals from different manufacturers, of different ages and agglomeration degree, which contained either Standard AOX or Super AOX.

The conditions of all the tests were the following:

Quantity of sample	:	60 grams
Oxygen initial pressure	:	60 psig
Temperature	:	100°C

Figure 2 shows the results for fish meal manufactured by Empresa Pesquera Tocopilla. The average slopes of the respective curves, expressed in psi/hour are:

Age of the sample (days)	Standard AOX	Super AOX
240	-3.25	-11.71
285	-8.38	-13.39

Figures 3, 4 and 5 show the results for fish meal manufactured by Pesquera Eperva, with different ages, kind of antioxidant and degree of agglomeration. The average slopes are shown in Figure 6.

2. Optimization of the conditions for tests in the oxygen bomb

2.1. Characteristics of fish meal samples

	Antioxidant	Age of sample (days)
Sample 1	Standard	150
Sample 2	Super	150
Sample 3	Standard	15
Sample 4	Without antioxidant	15
Sample 5	Standard	120
Sample 6	Standard	60
Sample 7	Standard	45

2.2. Self-combustion tests

Sample No.	Oxygen Pressure (psig)	Initial comb. T° (°C)	Max. T°
3	60	174	790
4	60	176	814
3	80	164	740
4	80	167	610

2.3. Tests in the oxygen bomb

For then same fish meal, different tests were carried out to determine the influence of the following variables of the process in the oxygen bomb.

- Initial pressure
- Temperature of the test
- Quantity of fish meal loaded into the bomb.

The corresponding results are shown in Fig. 7, 8 and 9.

Based on the results obtained, two additional series of tests were performed for each of the fish meal samples. In the first series the oxygen bomb's official operating conditions were used, that is, initial pressure: 60 psig, temperature: 100°C, quantity: 60 grams.

In the second series, the same initial pressure was maintained, put the temperature was increased to 120°C, and the quantity of the samples was reduced to 40 grams, which significantly shortened the process time to approximately 2 hours.

The results corresponding to samples 2, 4 and 5 are shown in Figures 10, 11 and 12, respectively. Figures 13 and 14 show the comparative results of all the samples for the two series of test conditions.

FISH MEAL STABILITY CRITERIA

The criterion adopted in Perú to establish stability of fish meal to oxidative degradation processes, is that the rate at which the pressure of oxygen drops in the bomb may not be more than 10 psi/hour from the moment it reaches its maximum value, when its temperature rises from room temperature to the bath's temperature. This has the disadvantage that the duration of the test is rather long, usually about 3.5 hours.

The analysis of the results obtained when the oxygen bomb's test conditions are changed with the purpose of reducing its duration and which are summarized in Figure 14, make it possible to establish that the previous stability criterion was not a valid one because there are not any significant differences in the pressure reduction rate for different fish meal samples with different antioxidants, as it occurs when the original conditions are used, which can be clearly seen in Figure 13.

This makes it necessary to adopt new criteria for determining fish meal stability.

1. Stability criterion : time of return

Corresponds to the time required for pressure to return to its original value, that is 60 psig for the series of tests reported here.

The results shown in Figures 13 and 14 are summarized in the following table:

Sample No.	Type of Antiox.	Average slope Orig. cond. (psi/hr)	Time of return Modified cond. (minutes)
2	Super	-11.4	66
3	Standard	-2.9	123
4	without AOX	-11.6	56
5	Standard	-5.6	94
6	Standard	-5.8	97
7	Standard	-3.6	78

It can be seen that the stability criterion based on the pressure reduction rate is met only by fish meals which had been added the standard antioxidant.

The values shown in the above table clearly indicate significant differences in the time of return, which make it possible to use this time as a fish meal stability criterion when oxygen bomb tests are carried out under modified conditions to permit to reduce its duration.

The maximum value of the time of return which reliably indicates that a fish meal is or not stabilized requires carrying out a larger number of tests before this procedure can be officialized.

2. Stability criterion : area under the curve

Upon observing the pressure - time curves for the different fish meal samples shown in Figure 14, which correspond to modified conditions of the oxygen bomb tests, it is possible to see that the fish meal without antioxidant (sample 4) shows a maximum considerably lower than the other samples, as well as a sharper drop of pressure. This suggests that the area under the curve can be used as an alternative stability criterion.

The interval of time necessary to determine this area is arbitrary, but it seems reasonable to consider the time between the test's initiation time zero and a final time similar to the total duration of measurements, which for the series of new conditions proposed has been set at 120 minutes.

The following results are the ones obtained for the six samples:

Sample No.	Type of Antiox.	Average slope Orig. cond. (psi/hr)	Area under curve Modified cond. (psi.minutes)
2	Super	-11.4	7578
3	Standard	-2.9	8458
4	without AOX	-11.6	7253
5	Standard	-5.6	7997
6	Standard	-5.8	8164
7	Standard	-3.6	7945

The observation mentioned before about the need to carry out a larger number of tests to provide a basis for this possible stability criterion, is valid.

CONCLUSIONS

It has been established that the oxygen bomb method is feasible to determine fish meal stability to oxidation by means of many tests carried out with different kinds of fish meals.

Comparison between two antioxidants using this procedure, indicates that the mixture of 33% etoxiquin and 67% BHT and lecithin is less effective than pure etoxiquin.

It is possible to optimize the method regarding duration, by performing the test under different conditions than the ones used at present. The adoption of new conditions for the oxygen bomb test makes it necessary to establish new fish meal stability criteria, which will have to be validated by means of a large number of tests.

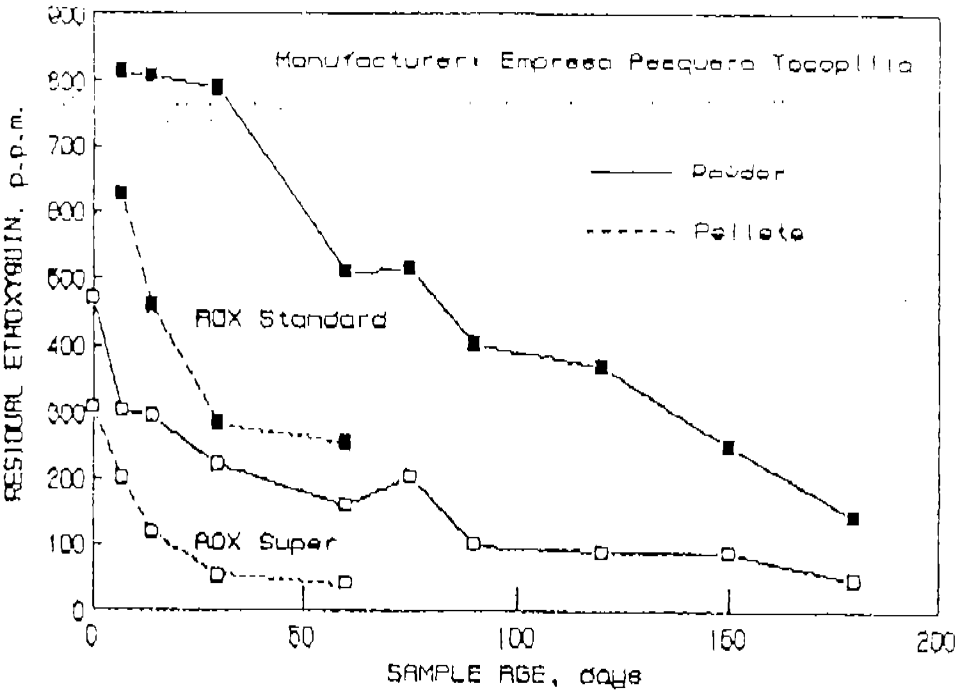

Fig. 1. Residual ethoxyquin content for powdered and pelletized samples with two types of antioxidants.

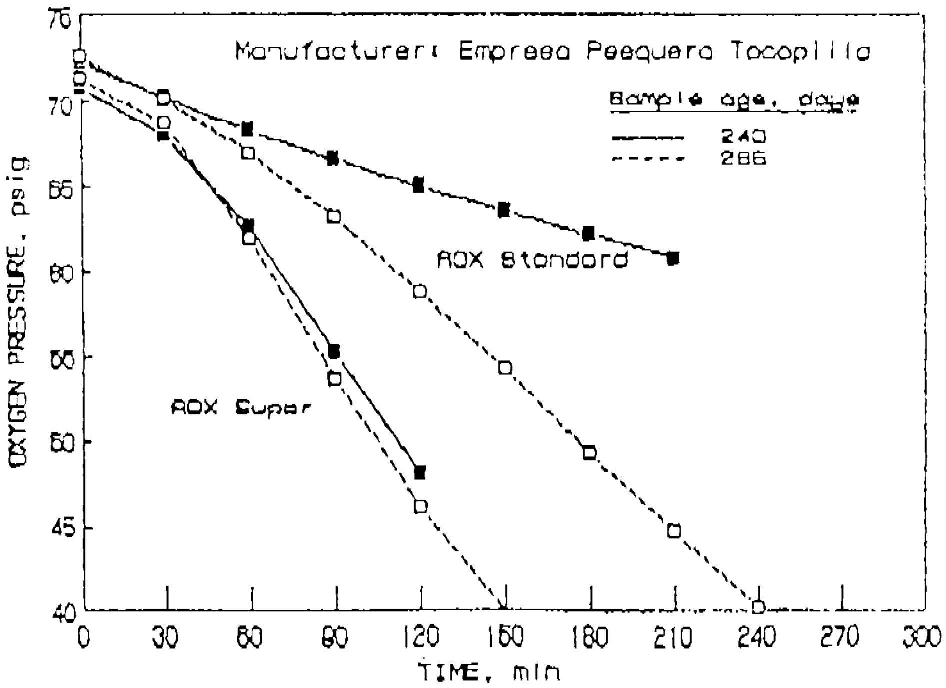

Fig. 2. Oxygen bomb tests for samples of two ages with two types of antioxidants.

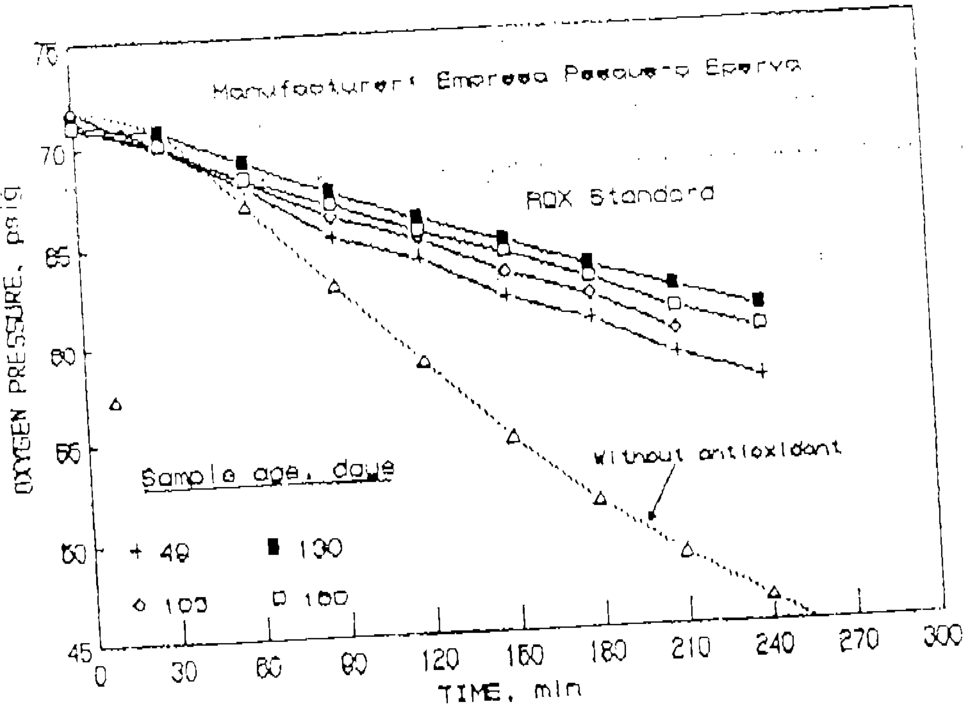

Fig. 3. Oxygen bomb tests for samples of four ages with AOX Standard antioxidant.

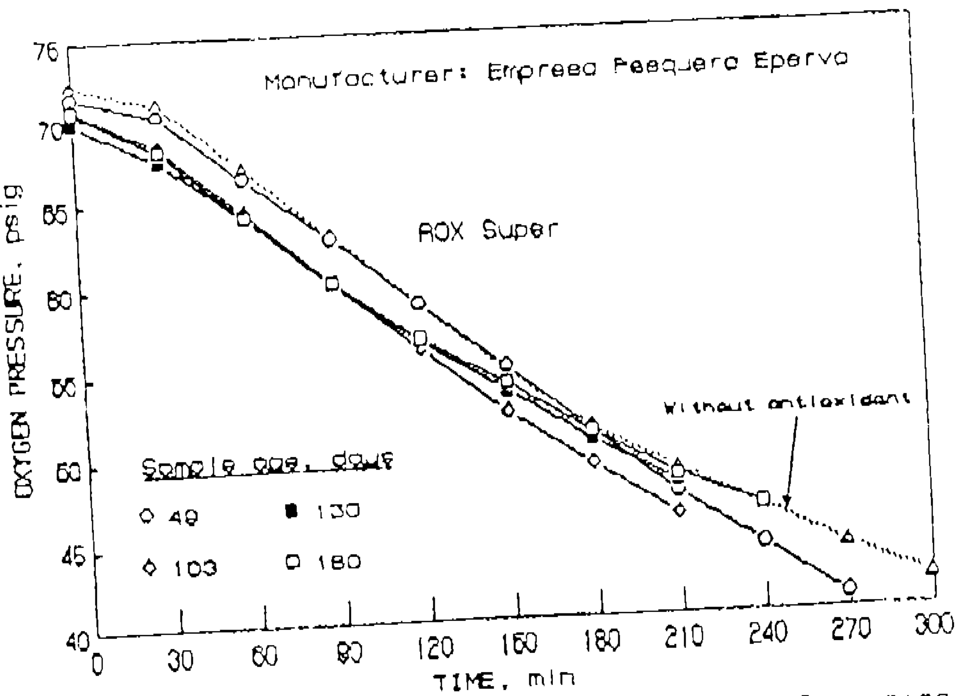

Fig. 4. Oxygen bomb tests for samples of four ages with AOX Super antioxidant.

END

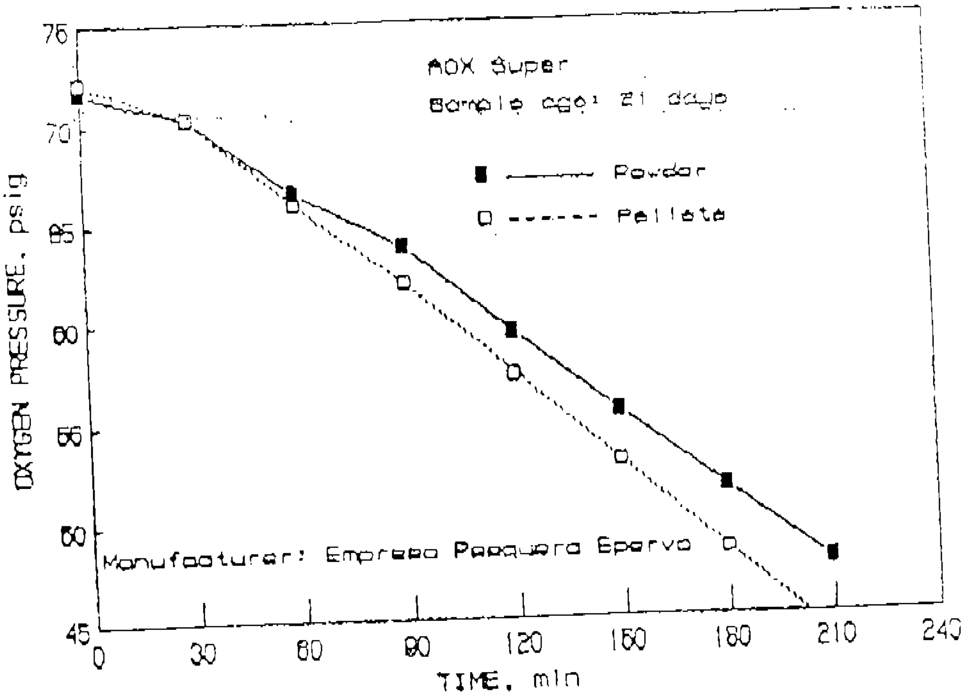

Fig. 5. Oxygen bomb tests for powdered and pelletized samples with AOX Super antioxidant.

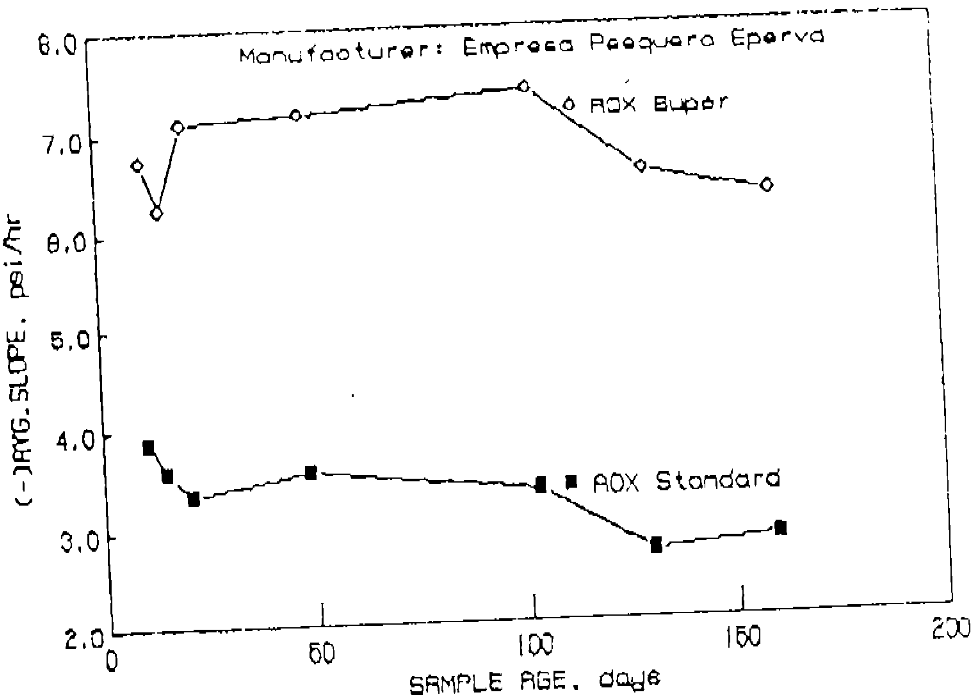

Fig. 6. Average slope vs. sample age, with AOX standard and AOX Super antioxidants.

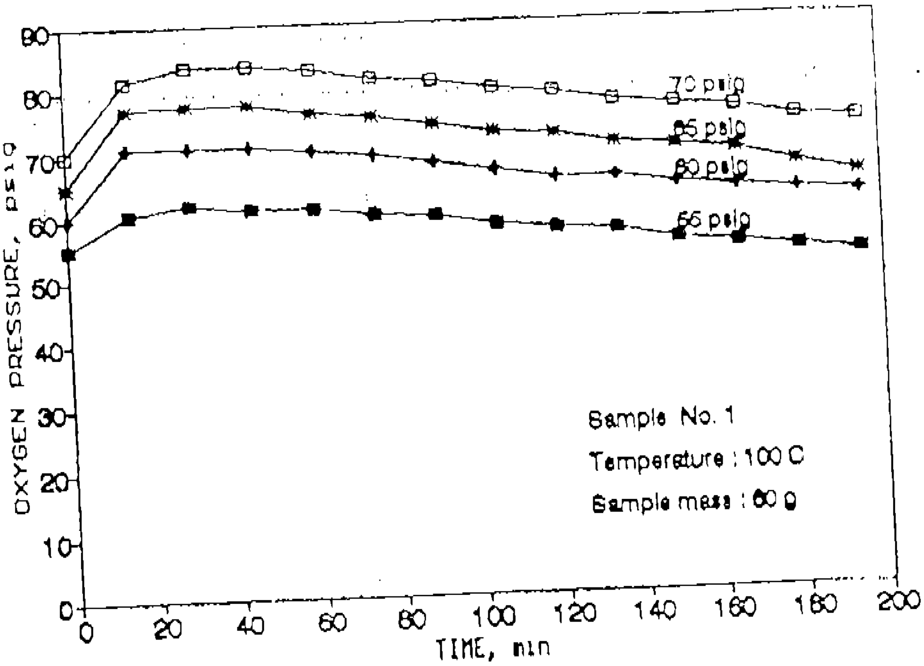

Fig. 7. Effect of initial oxygen pressure on oxygen bomb tests.

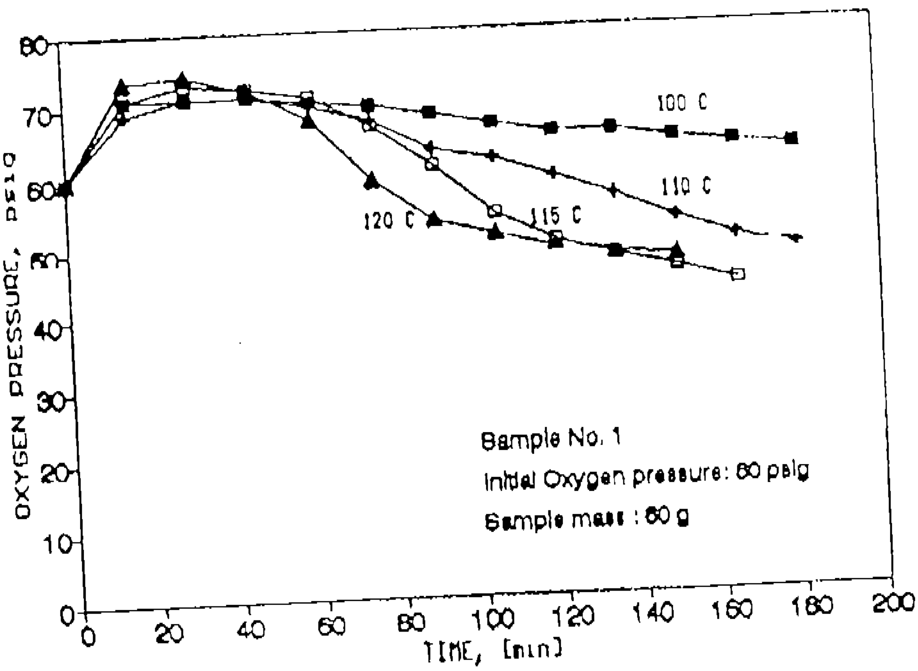

Fig. 8. Effect of temperature on oxygen bomb tests.

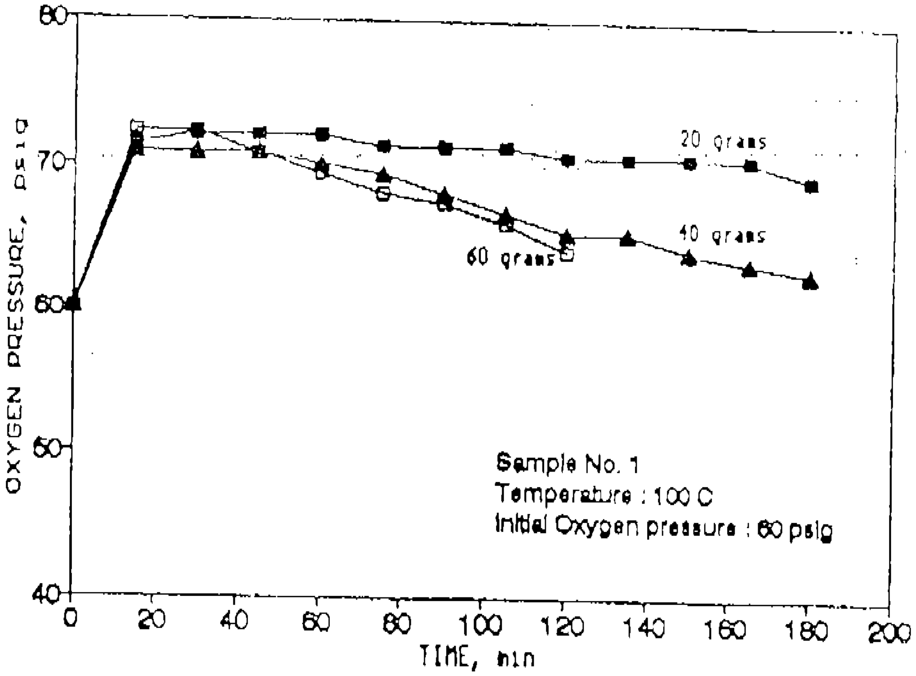

Fig. 9. Effect of sample mass on oxygen bomb tests.

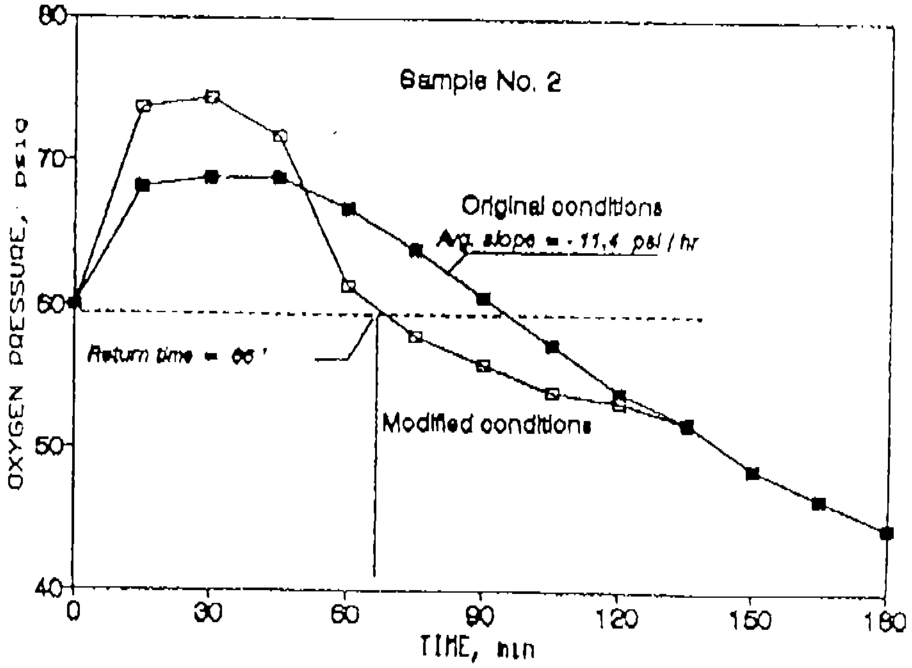

Fig. 10. Comparison of oxygen bomb test conditions for samples with AOX Super antioxidant.

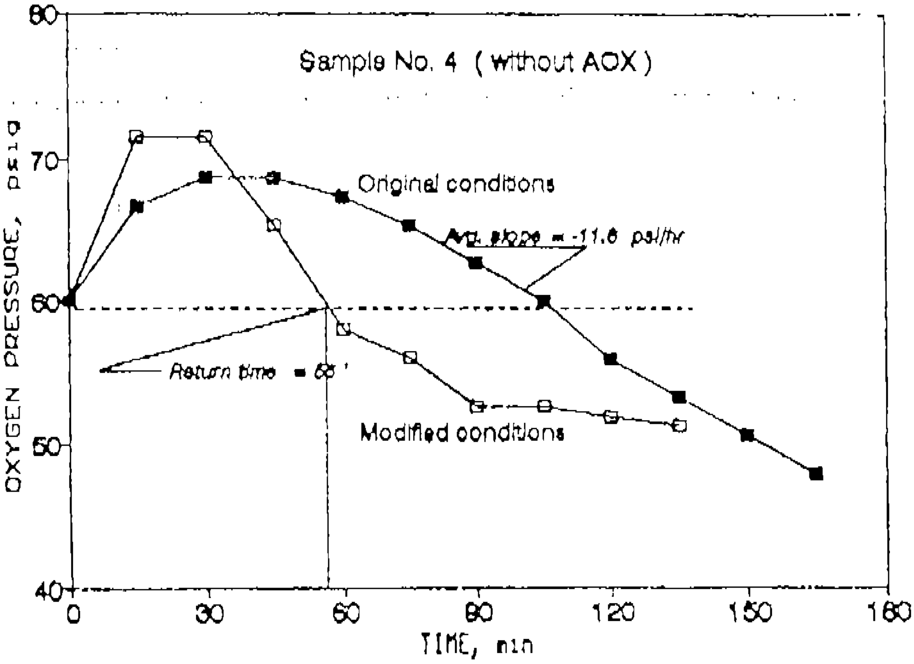

Fig. 11. Comparison of oxygen bomb test conditions for samples without antioxidant.

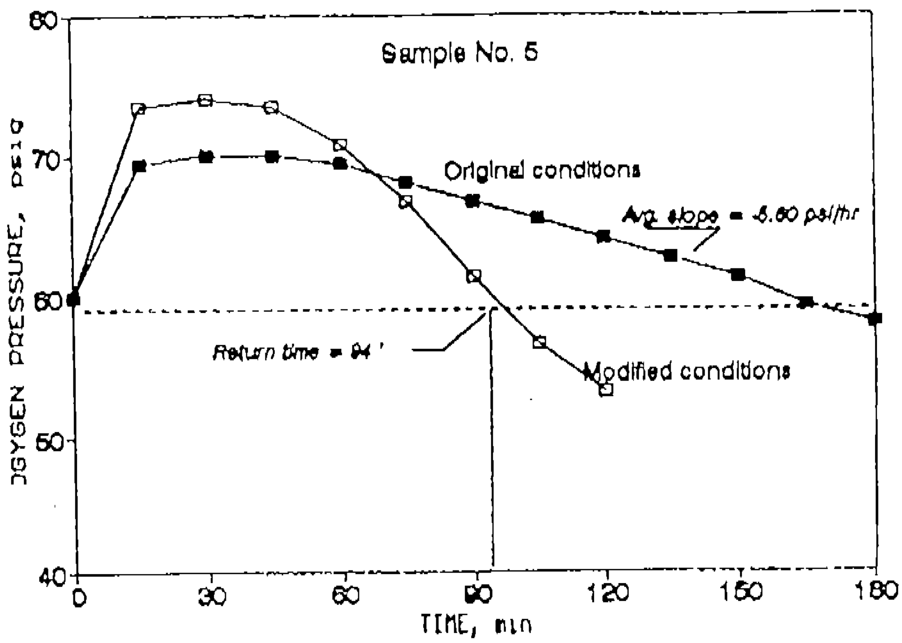

Fig. 12. Comparison of oxygen bomb test conditions for samples with AOX Standard antioxidant.

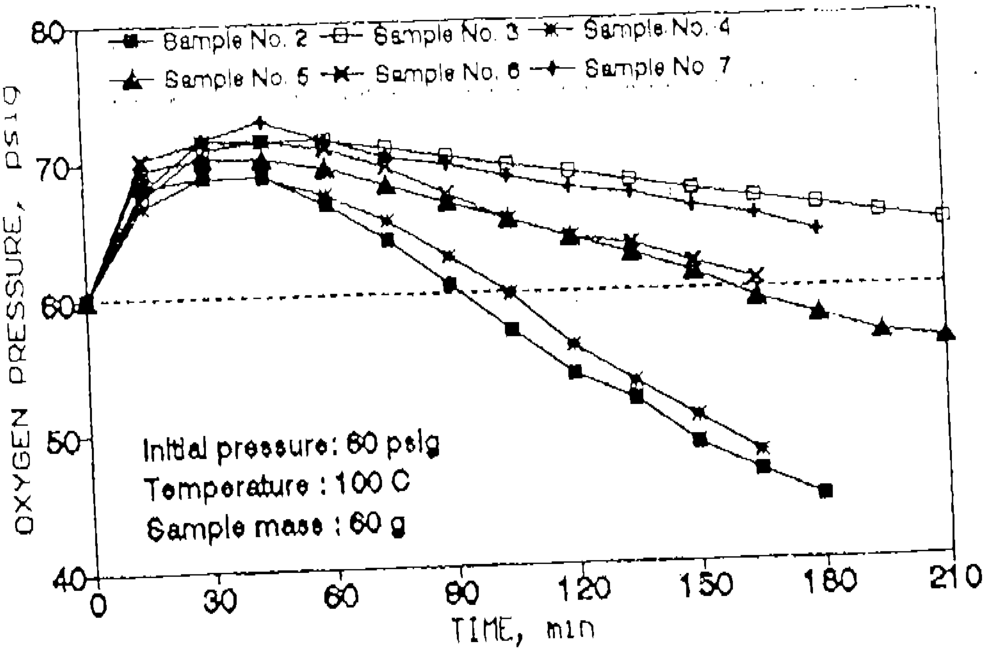

Fig. 13. Oxygen bomb tests with original conditions for six samples.

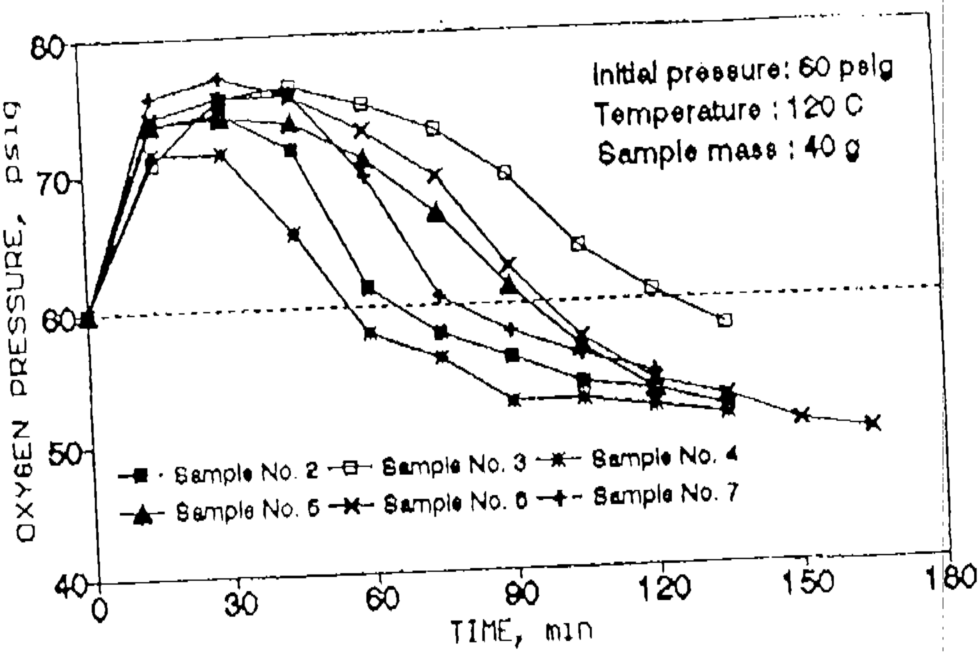

Fig. 14. Oxygen bomb tests with modified conditions for six samples.

END