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FIELD FAILURE ANALYSIS

BY

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INTRODUCTION

Compound reconstruction is the duplication of an unknown product by chemical means to give the new compound similar physical and chemical properties of the unknown compound. Three major reasons for reconstruction of a product are duplication, quality control, and for product failure.¹

When a product has failed in service, the analyst is asked to determine the cause of failure by chemical and physical means. Determining the cause of failure in a failed compound would include such tests as specific gravity, polymer identification, carbon black, ash, and extractable content. If this testing indicates the formulation falls within quality control specifications, then a more detailed analysis may be required such as plasticizer identification, antioxidants used, total sulfur, wax content, etc. If this testing shows that the proper ingredients were used, the analyst begins to feel a little "boxed in" as to why the product failed.

The purpose of this paper is to show that infrared analysis can differentiate between various environmental causes of polymer degradation. The paper will also provide a set of infrared spectra demonstrating how infrared shows the various changes which occur.

EXPERIMENTAL

Three different rubber formulations in tables one through three were mill mixed and cured. A Monsanto Rheometer was used to determine the cure time.

Cured slabs were put into solution according to ASTM D3677 using ortho-dichlorobenzene as the solvent.² Films were cast on Potassium Bromide plates and infrared spectra were made of each formulation. No extraction was made on the rubber formulations prior to solution.

Each formulation was then subjected to oxygen, ultraviolet radiation, heat and ozone, and a spectrum was made periodically to observe changes in the rubber structure. No attempt will be made to define what chemically changed the spectrum or caused new peaks to appear except in general terms.

RESULTS AND DISCUSSION

In general, several control spectra were made in succession of each formulation. After aging for a period of time, new spectra were made and put on the control spectra so that any change could be easily observed. Mixed conditions such as ultraviolet radiation and heat or oxygen and ozone are not included in this paper. One actual field example will be demonstrated.

NATURAL RUBBER - HEAT AGING AT 100°C - ASTM D573

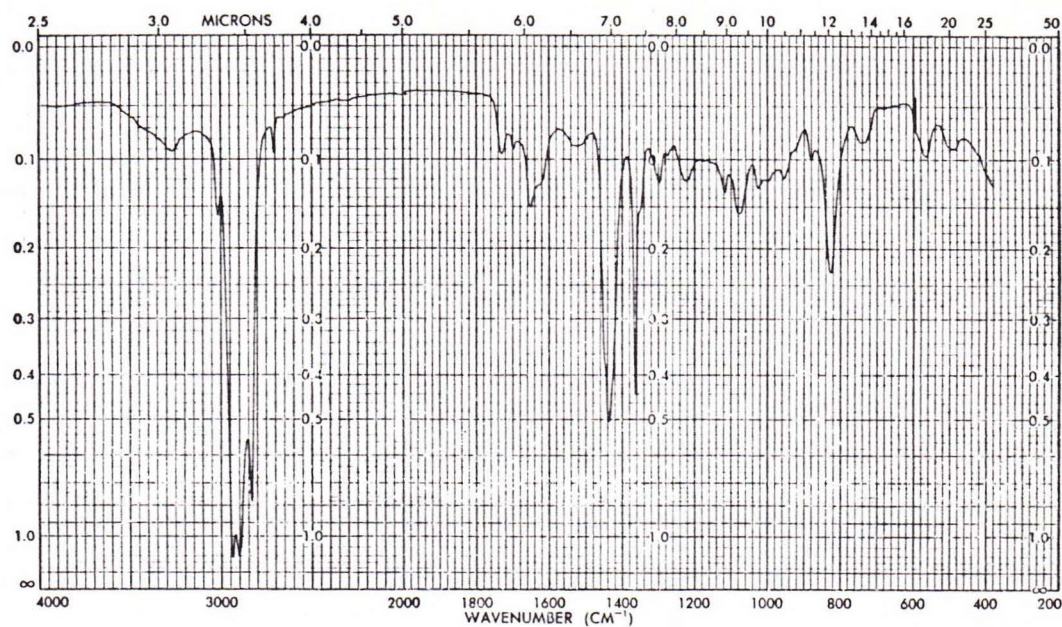


Plate 1 - CONTROL

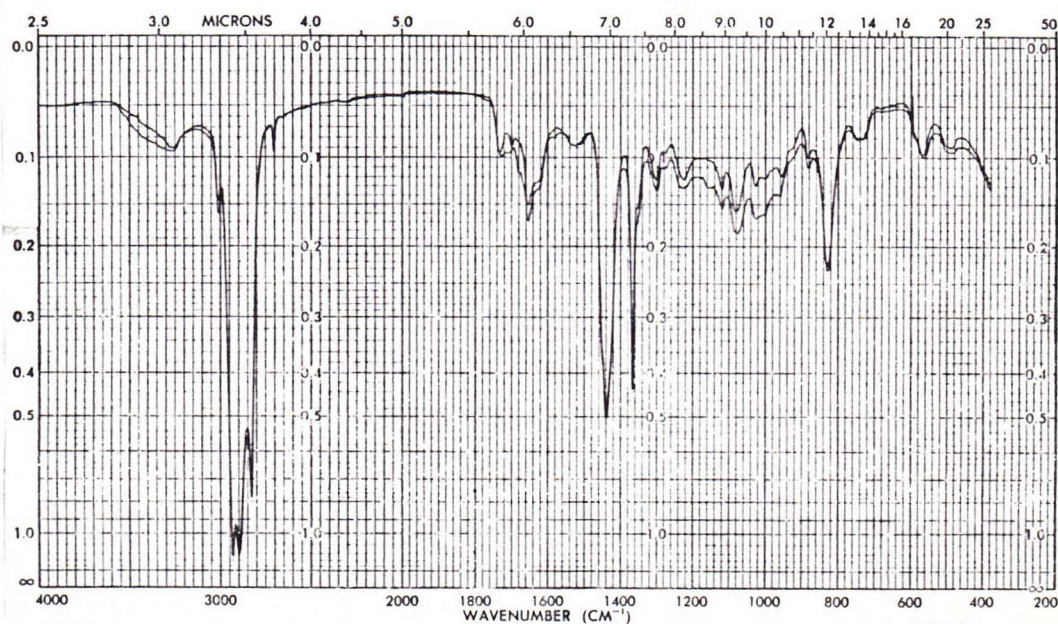


Plate 2 - 24 hr. at 100°C: Some changes are observed from 1450cm^{-1} to 850 cm^{-1} in that base line has lowered. Generally this occurs in most spectra of degraded products. Notice the formation of a new peak at 1160cm^{-1} . This peak will not occur in the oxygen or ozone agings.

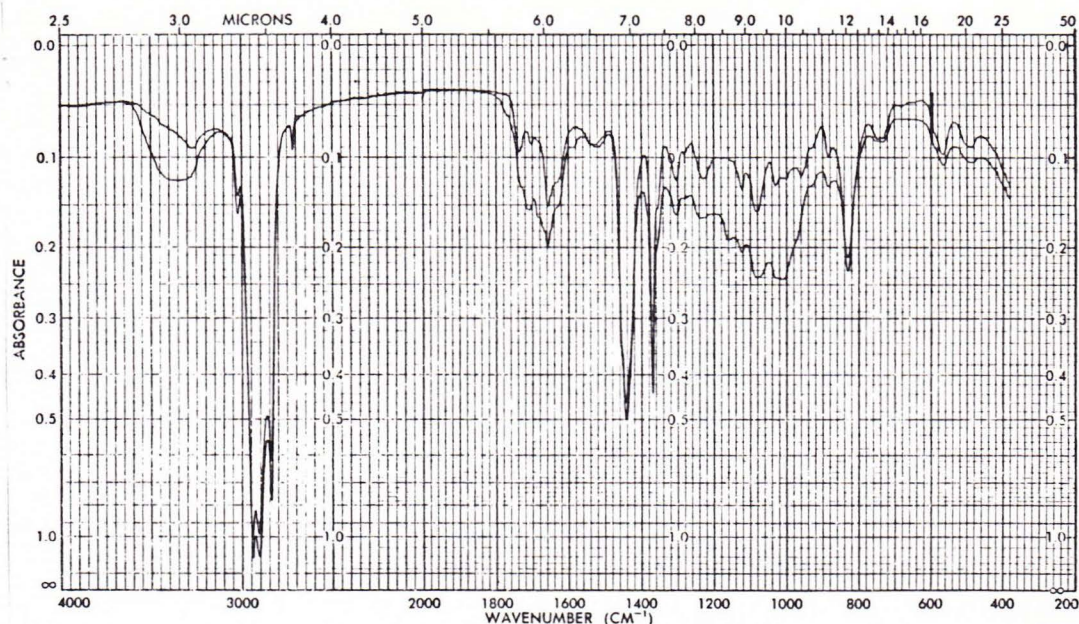


Plate #3 - 48 hrs. at 100°C: The sample begin to pick up moisture as shown at 3350 cm^{-1} . Some loss of hydrocarbon peaks become apparent by the loss of absorption around 2900 cm^{-1} and 1440 cm^{-1} . Increased oxidation is occurring by absorption occurring from 1660 cm^{-1} to 1720 cm^{-1} along with the loss of base line. The new formed peak at 1160 cm^{-1} is now clearly seen.

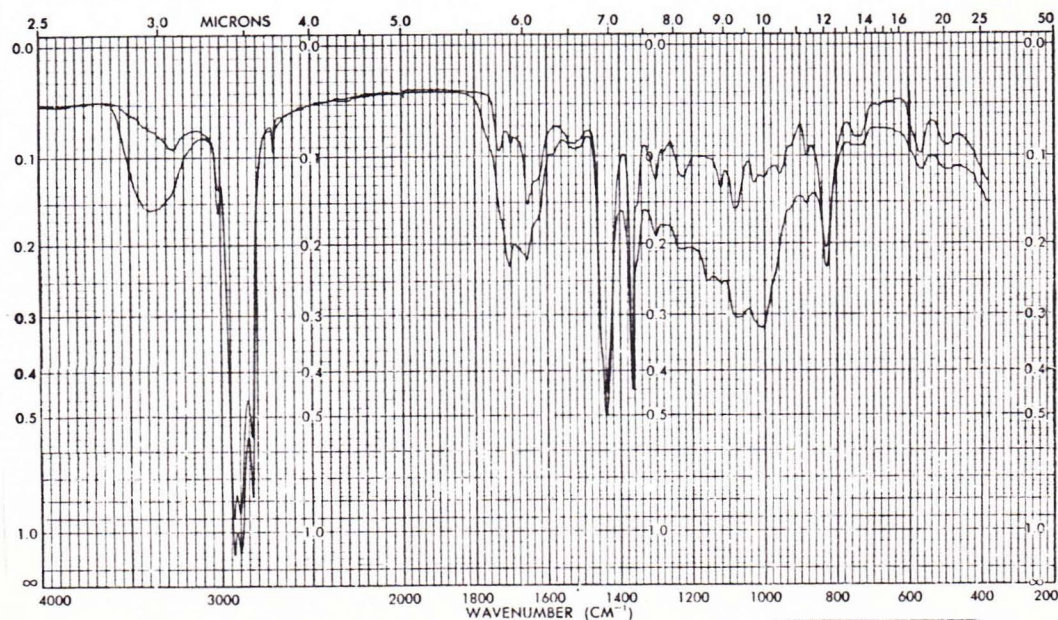


Plate #4 - 72hrs. at 100°C: This spectrum is very similar to the natural rubber which was exposed 48 hrs. but much more predominate.

NATURAL RUBBER - OZONE At 50 pphm: 40°C, ASTM D1149

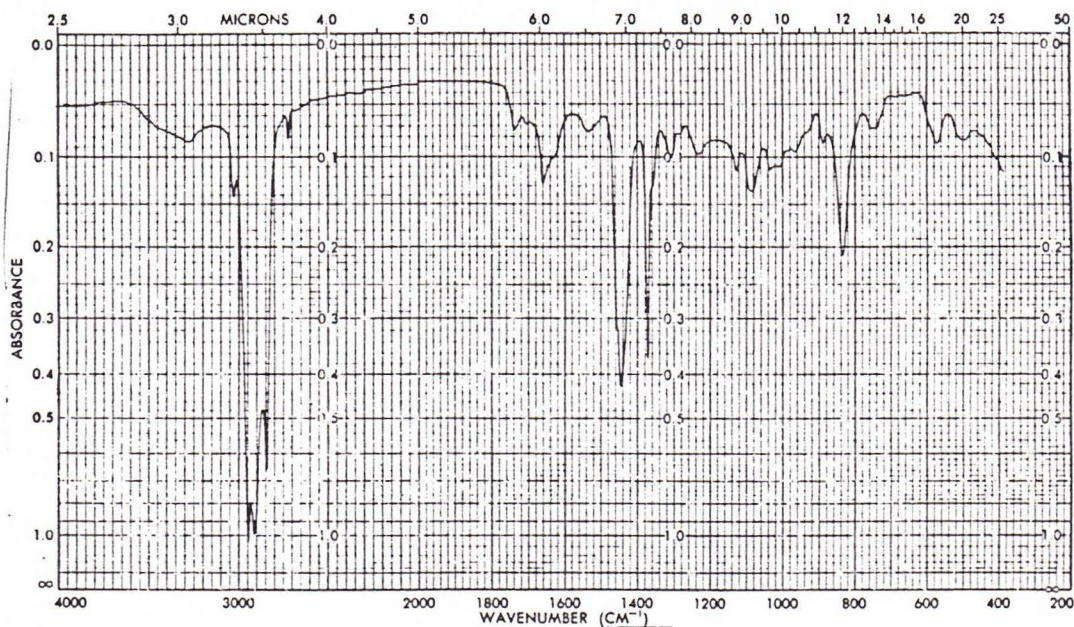


Plate #5 - CONTROL

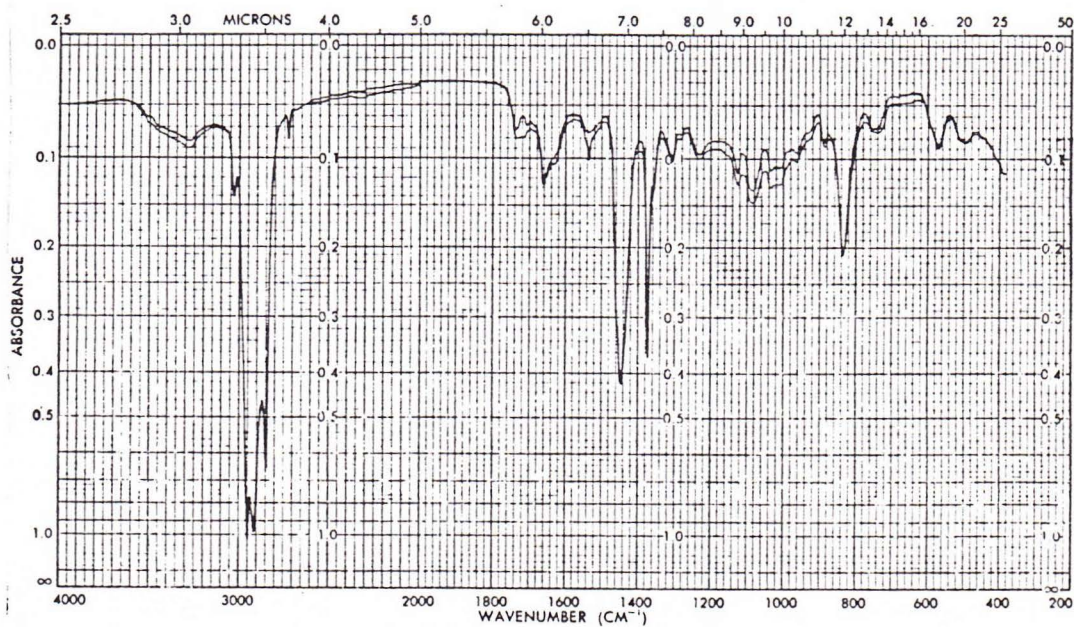


Plate #6 - 24 hrs. in ozone - some oxidation is taking place by reduction in base line from 1300 cm^{-1} to 880 cm^{-1} . A new peak is formed at 1530 cm^{-1} . This peak also will occur in the oxygen aging.

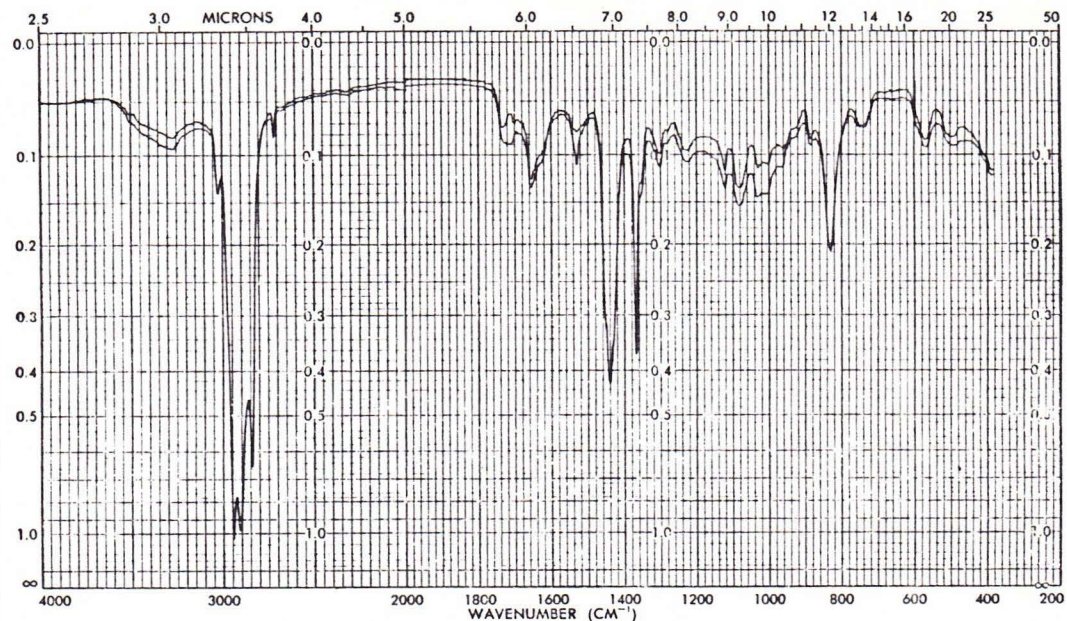


Plate #7 - 72 hrs. in ozone: This is the same as the 24 hr. aging with the difference in base line slightly greater.

NATURAL RUBBER - ULTRAVIOLET RADIATION - 40°C, ASTM D925

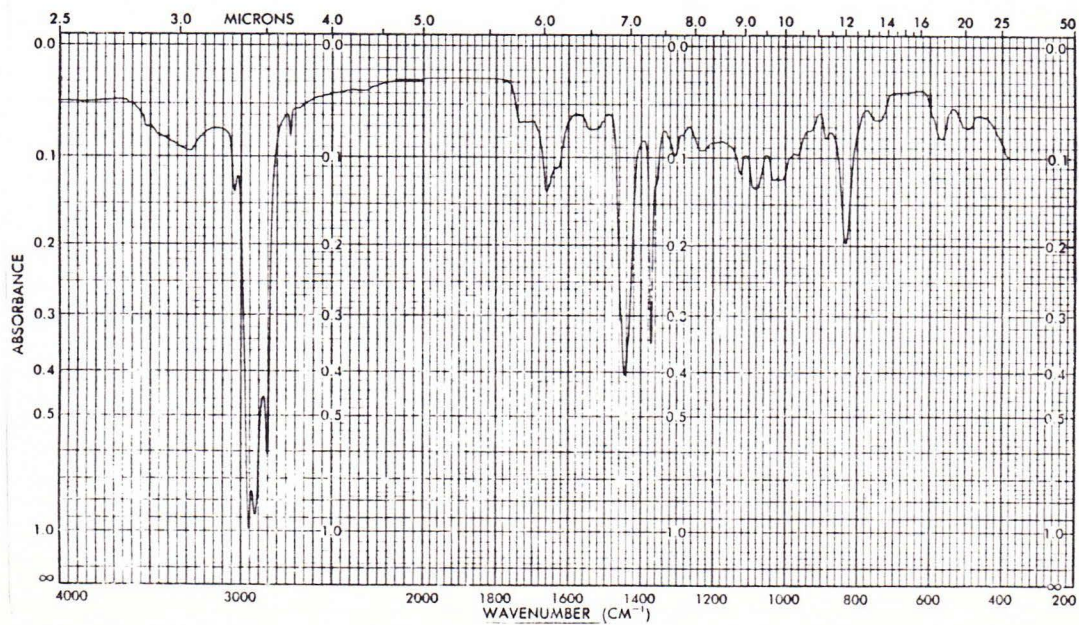


Plate #8 - CONTROL

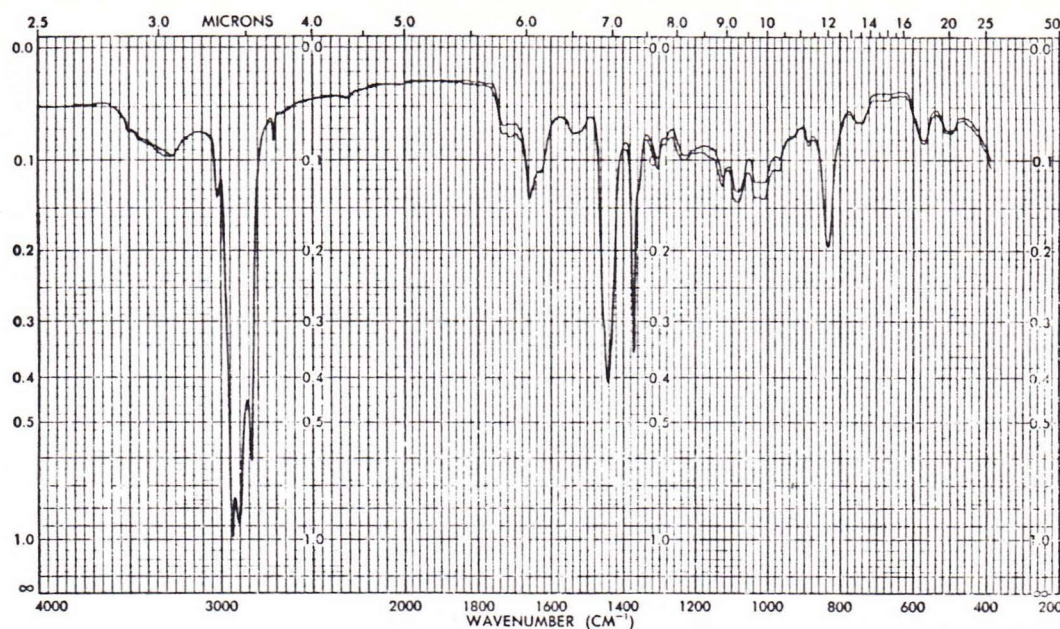


Plate #9 - One hr. under U.V. radiation: The spectrum is similar to the control and is included to show what an impact U.V. radiation can have on natural rubber compounds. The decrease in base line occurs from 960cm^{-1} to 1380cm^{-1} .

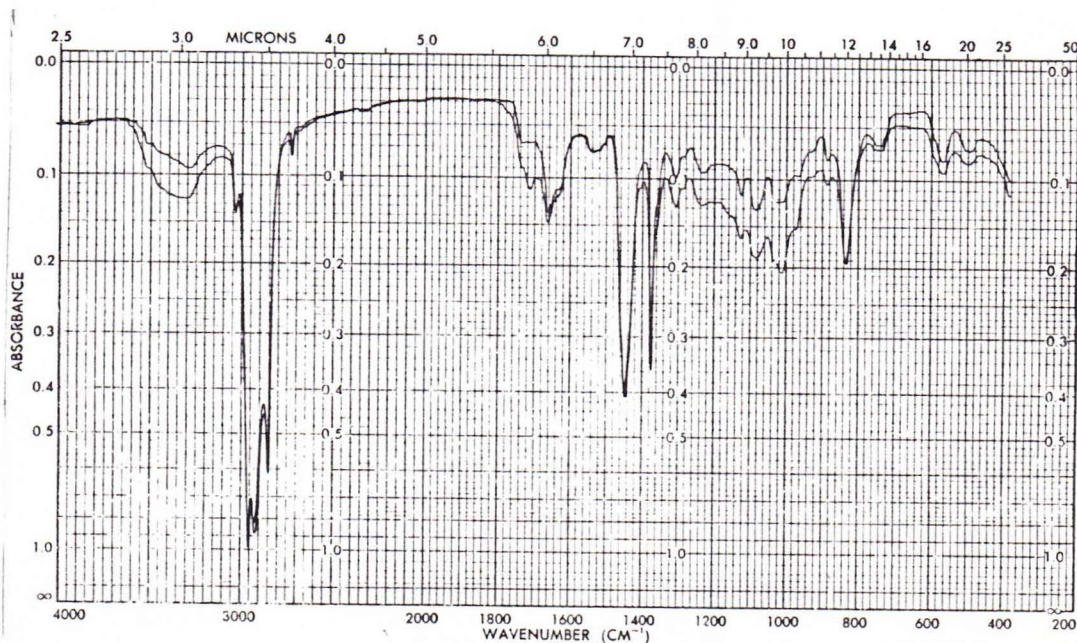


Plate #10 - 4 hrs. under U.V. radiation: Increased moisture is evident at 3350cm^{-1} . Increased oxidation is shown by the peak at 1710cm^{-1} and the decrease in base line.

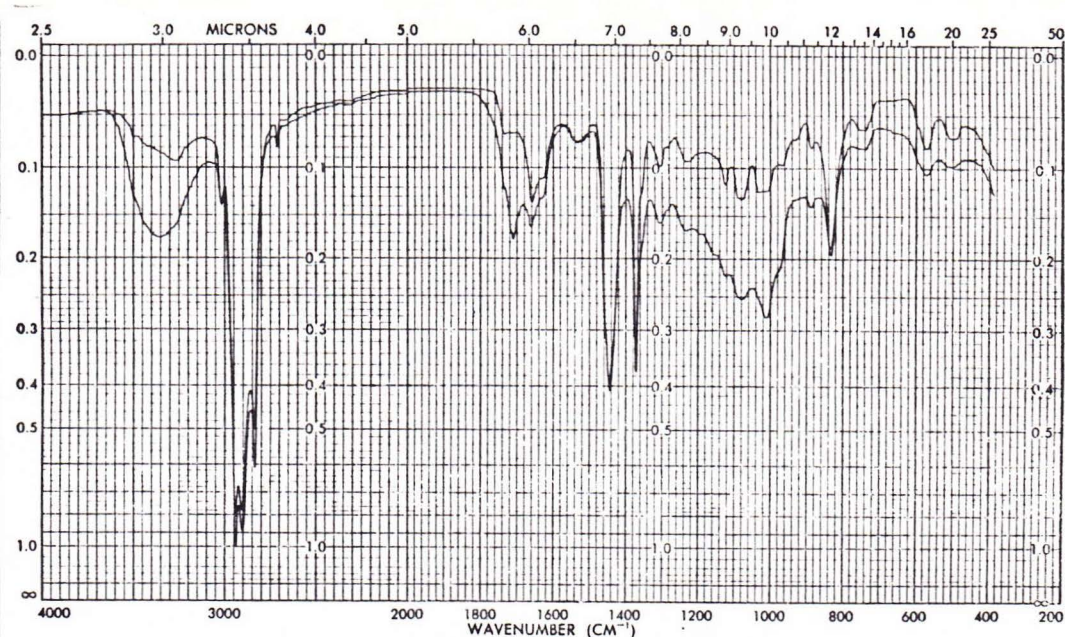


Plate #11 - 8 hrs. under U.V. radiation: This spectrum is similar to the 4 hr. spectrum but absorption is greater. Some loss of hydrocarbon function is observed at the 2900cm^{-1} region. The peak at 1035cm^{-1} is now missing and one is starting to form at 1160cm^{-1} .

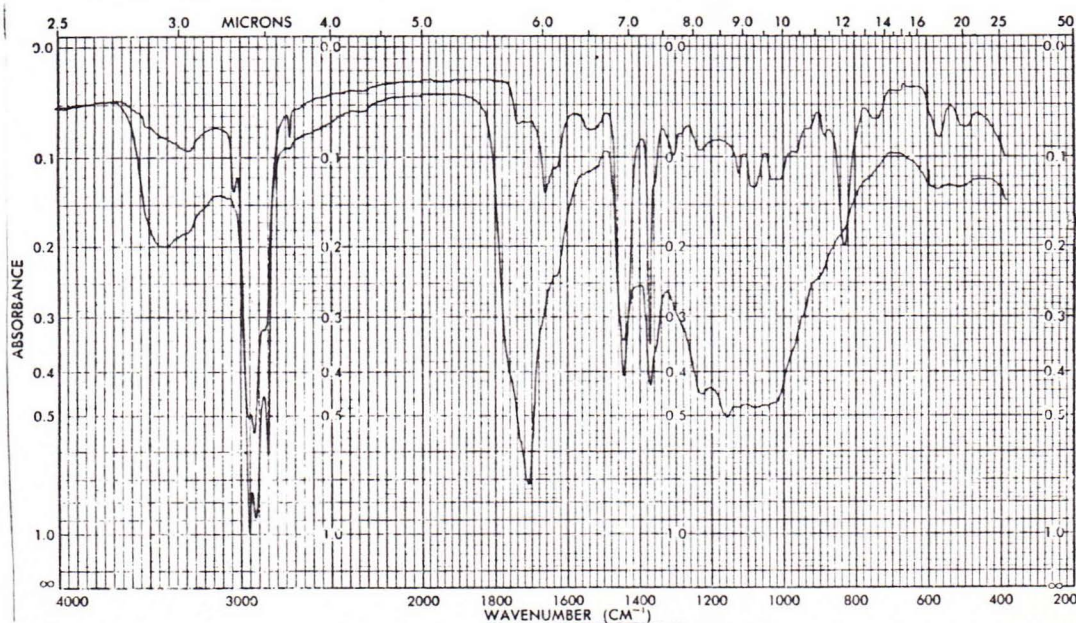


Plate #12 - 24 hrs. under U.V. radiation: Usually products have failed long before they have reached this state. Loss of hydrocarbon, gain in oxidation and loss of peaks are characteristic of this spectrum.

NATURAL RUBBER - OXYGEN PRESSURE AGING, 2100kPa, 70°C, ASTM D572:

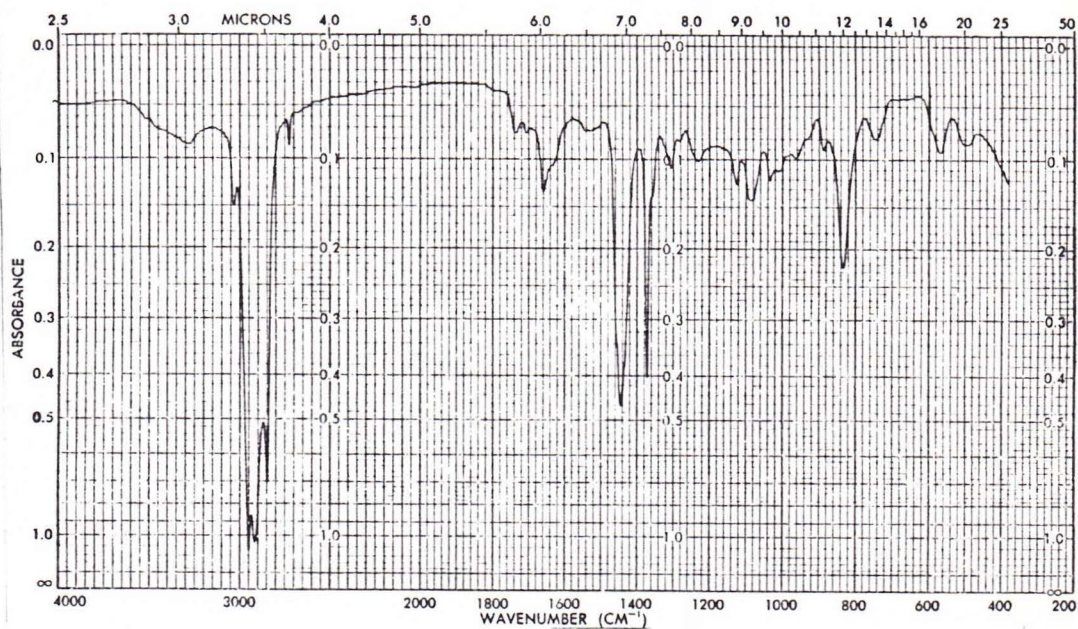


Plate #13 - CONTROL

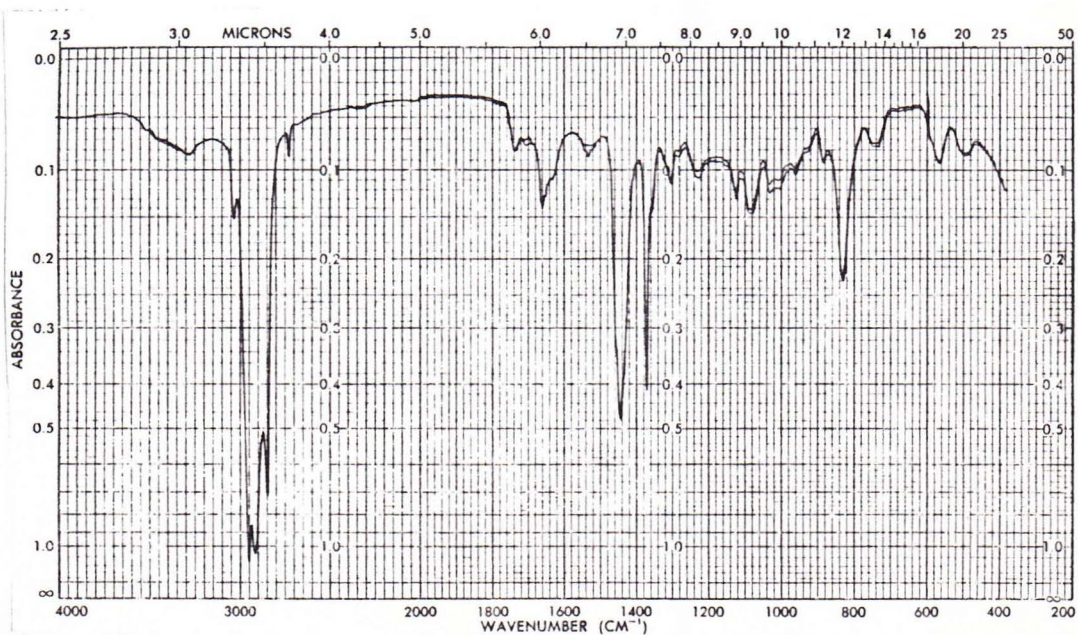


Plate #14 - 48 hrs. in oxygen: Small changes in base line are characteristic of all the spectra in this series from 880 cm^{-1} to 1300 cm^{-1} . A formation of a new peak at 1530 cm^{-1} is starting to occur.

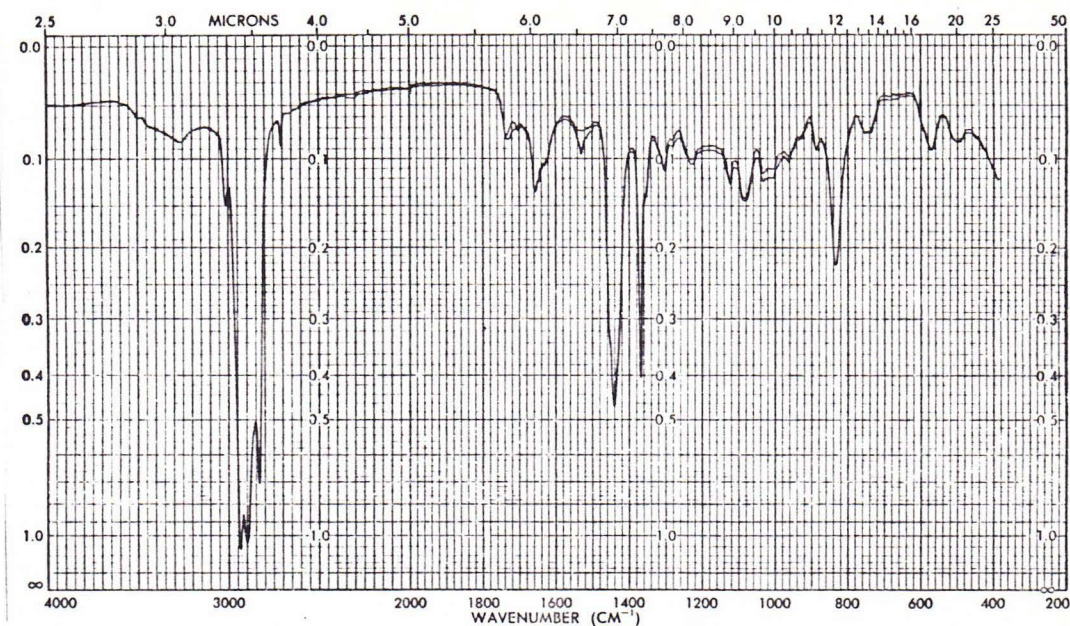


Plate #15 - 96 hrs. in oxygen: The new peak at 1530cm⁻¹ is more predominate.

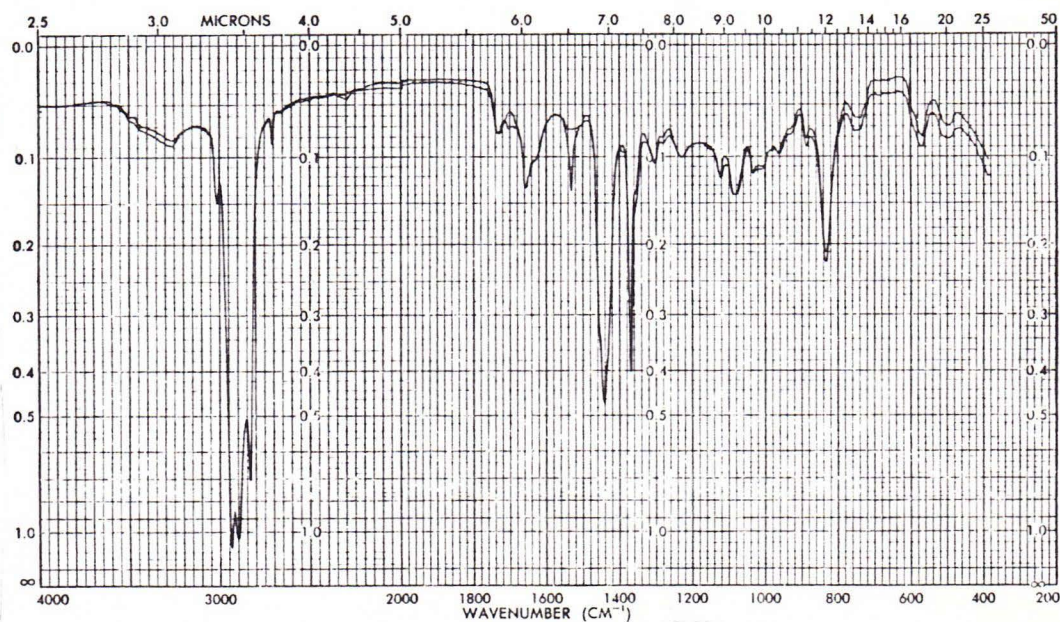


Plate #16 - 168 hrs. in oxygen: No major changes are observed with the exception of the absorption of the peak at 1530cm⁻¹.

DISCUSSION - NATURAL RUBBER

Of the different conditions imposed on Natural Rubber, it is shown that one could differentiate between heat and oxygen, heat and ozone, U.V. radiation and oxygen, or U.V. radiation and ozone. The spectra for oxygen and ozone have the same type of peak absorptions and can not be differentiated from each other. The same is true for the heat and U.V. radiation. Table IV shows the major changes which occur in the spectra for natural rubber.

POLYBUTADIENE RUBBER - HEAT AGING AT 150°C - ASTM D573

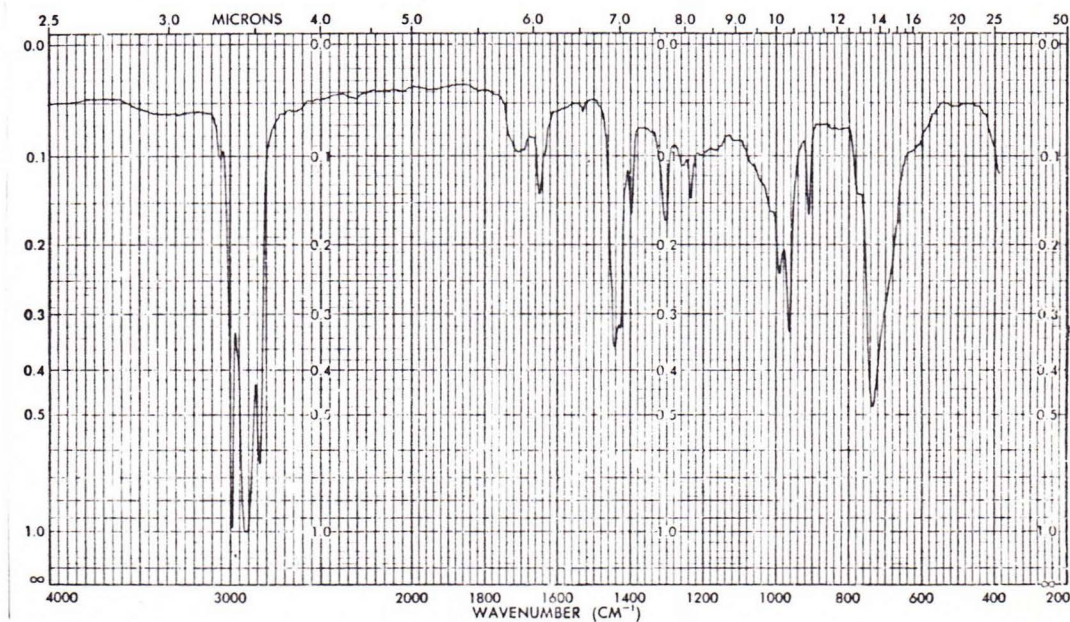


Plate #17 - CONTROL

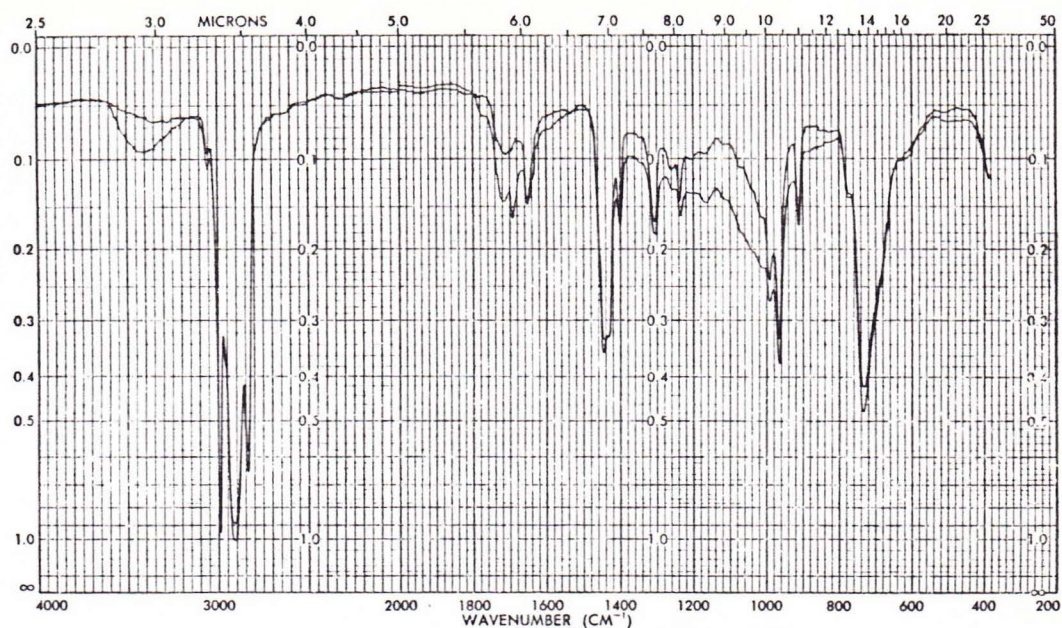


Plate #18 - 1 hour at 150°C: There is a loss in hydrocarbon structure at the 2900 cm^{-1} region. There is increased oxidation shown by the formation of two peaks at 1720 cm^{-1} and 1695 cm^{-1} and by the reduction in base line from 800 cm^{-1} to 1390 cm^{-1} . A new peak is forming at 1165 cm^{-1} .

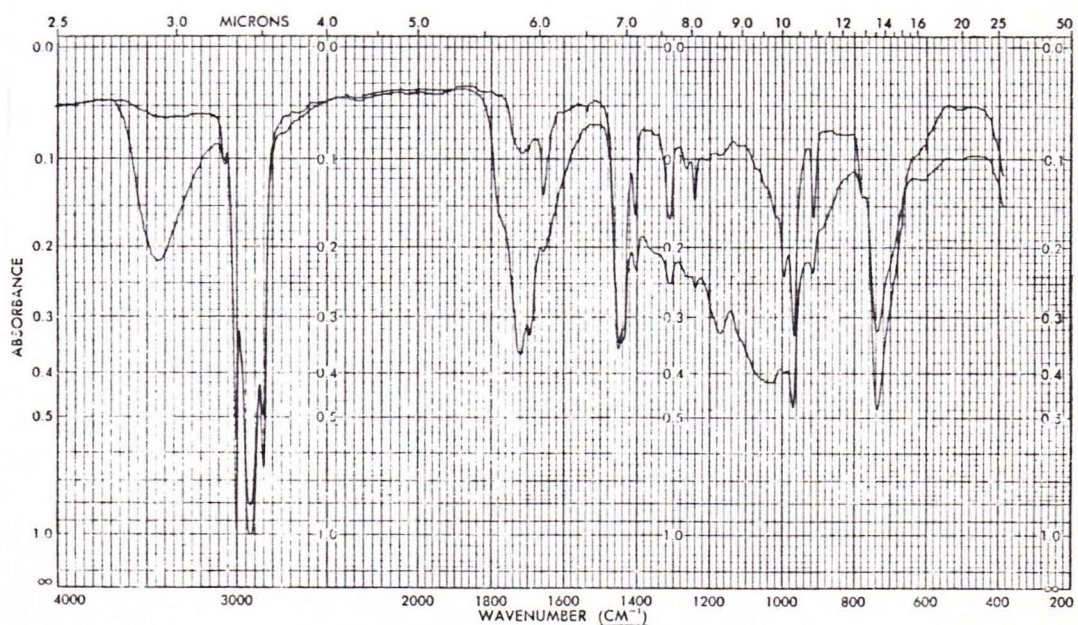


Plate #19 - 2 hours at 150°C: Again rubber products usually have failed before they would have reached this stage in degradation. The absorption at 1720 cm^{-1} and 1695 cm^{-1} is more evident as well as the peak at 1165 cm^{-1} . The absorption 1040 cm^{-1} is new as well.

POLYBUTADIENE RUBBER - OZONE AT 100 pphm - 40°C - ASTM D1149:

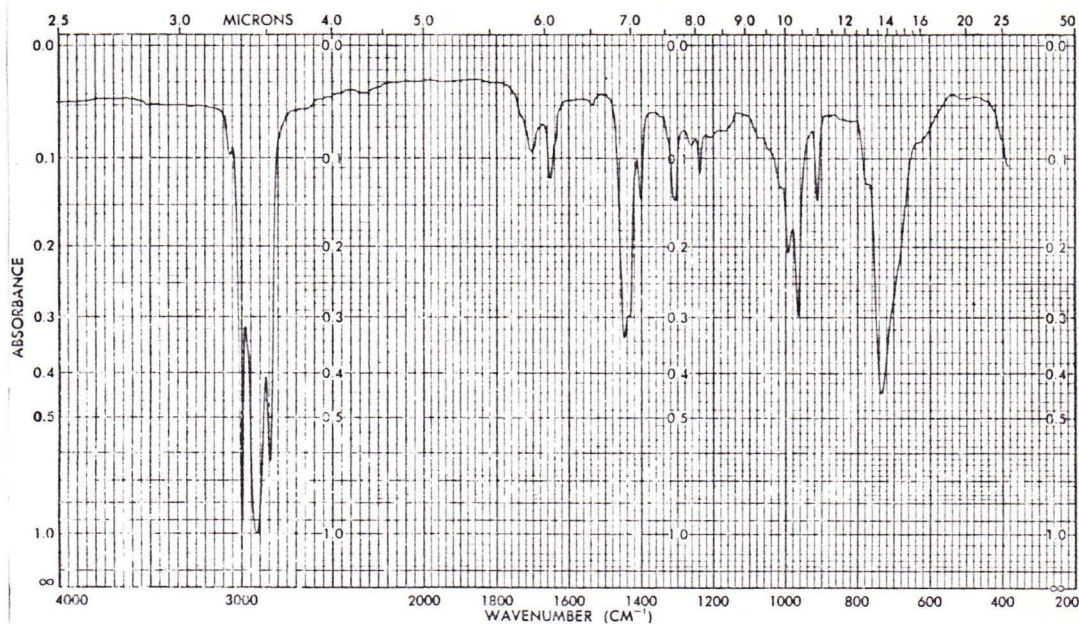


Plate #20 - CONTROL

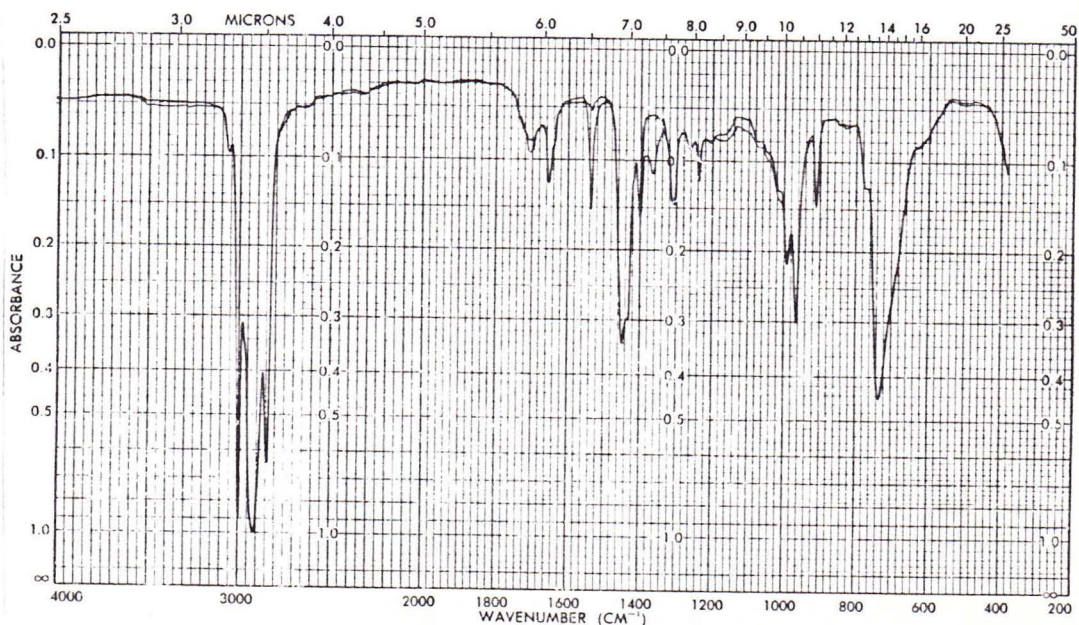


Plate #21 - 96 hours in ozone: Two major changes are observed. The first is the formation of the peak at 1535cm^{-1} . The second is a new formed peak at 1365cm^{-1} .

POLYBUTADIENE RUBBER - ULTRAVIOLET RADIATION AT 40°C - ASTM D925:

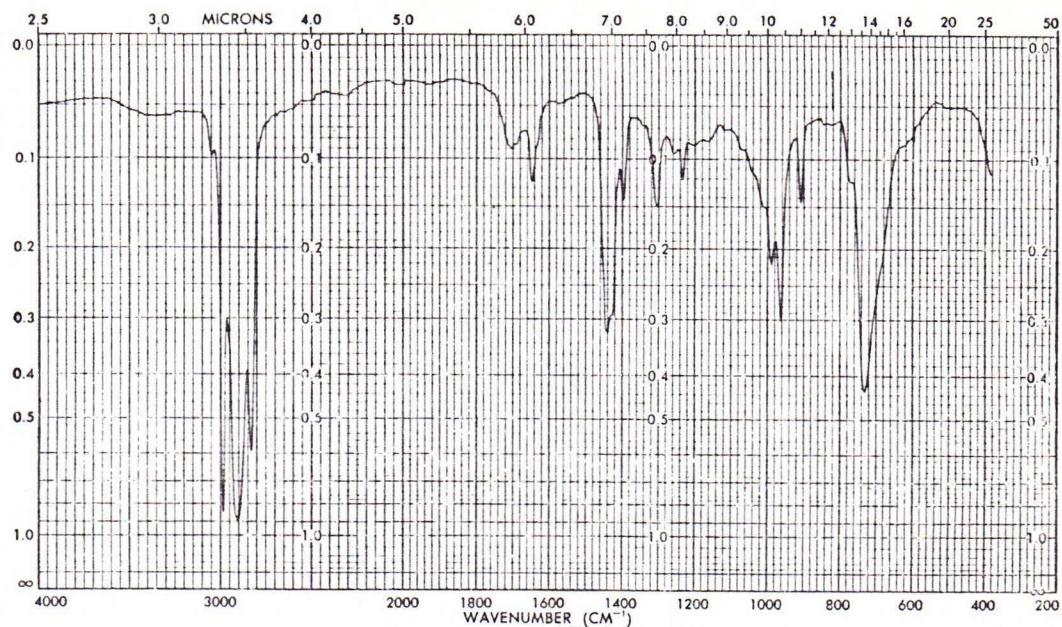


Plate #22 - CONTROL

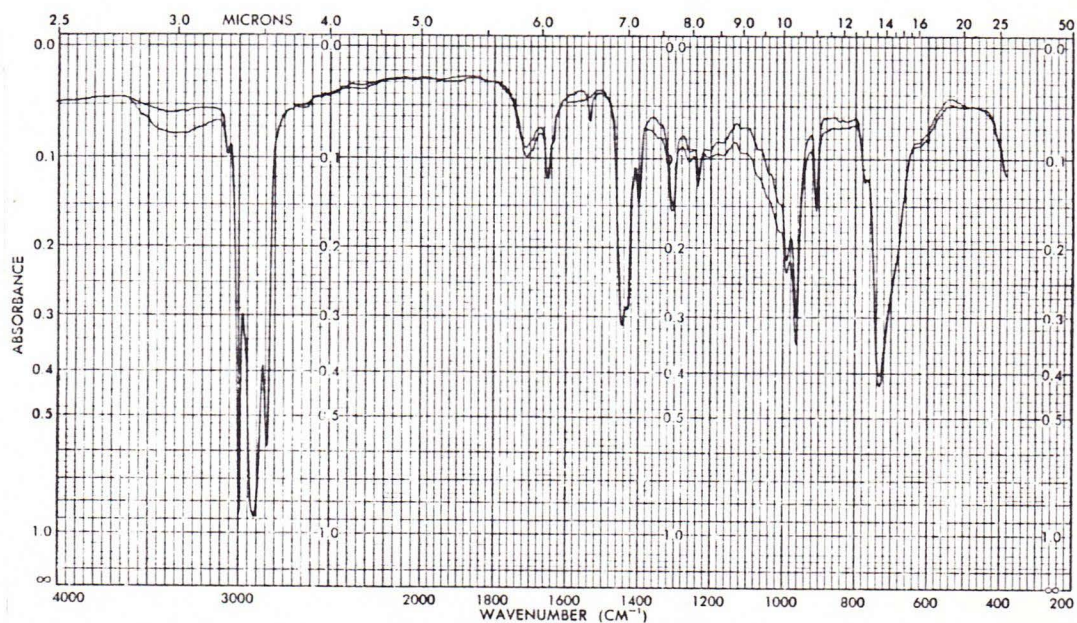


Plate #23 - 6 hours in U.V. radiation: The new formed peak at 1535cm^{-1} will tend to disappear as the aging period increases. Oxygen absorption is evident from the amount of absorption occurring at 1710cm^{-1} and the lowering of the base line from 200cm^{-1} to 1380cm^{-1} .

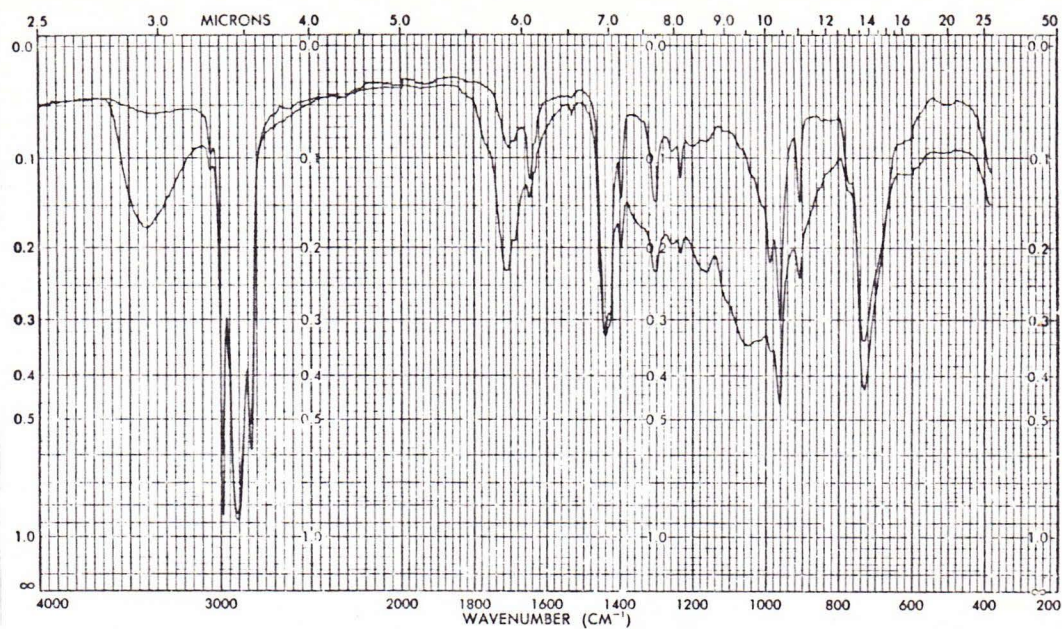


Plate #24 - 12 hours in U.V radiation: This spectrum is very similar to polybutadiene aged 2 hours at 150°C (Plate #19).

POLYBUTADIENE RUBBER, OXYGEN PRESSURE AGING 2100kPa, 70°C, ASTM D572:

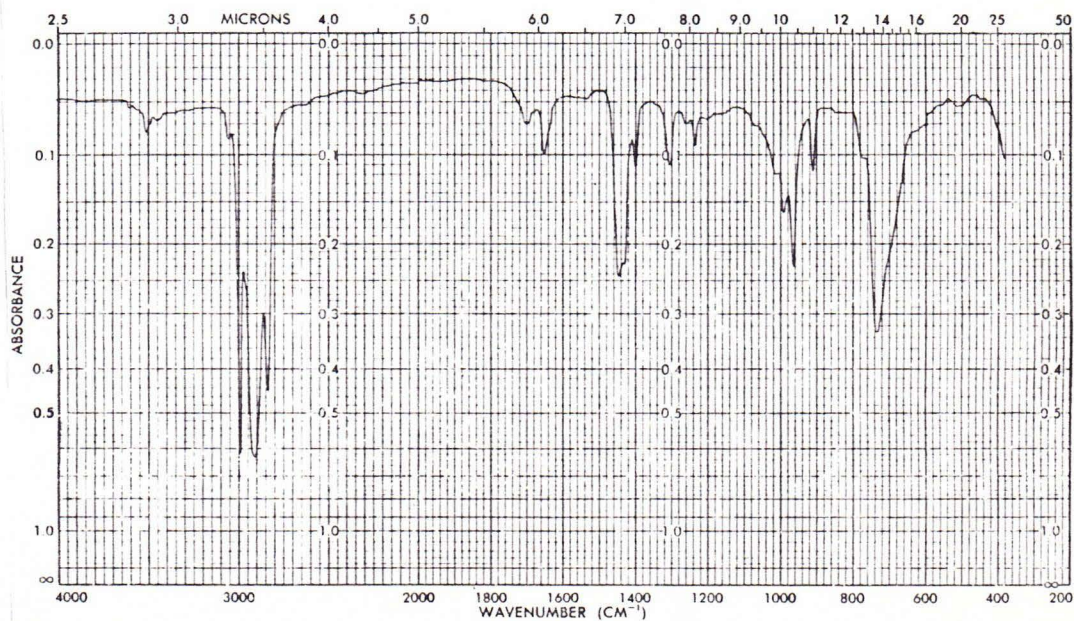


Plate #25 - CONTROL

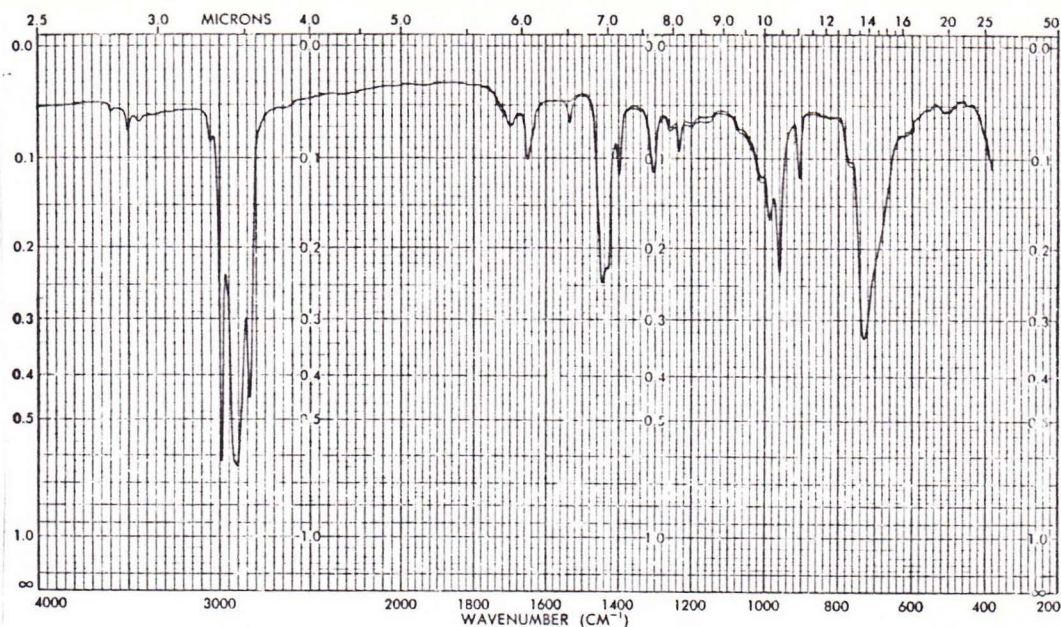


Plate #26 - 24 hours in oxygen: Other than a new peak forming at 1535cm^{-1} is virtually the same as the control.

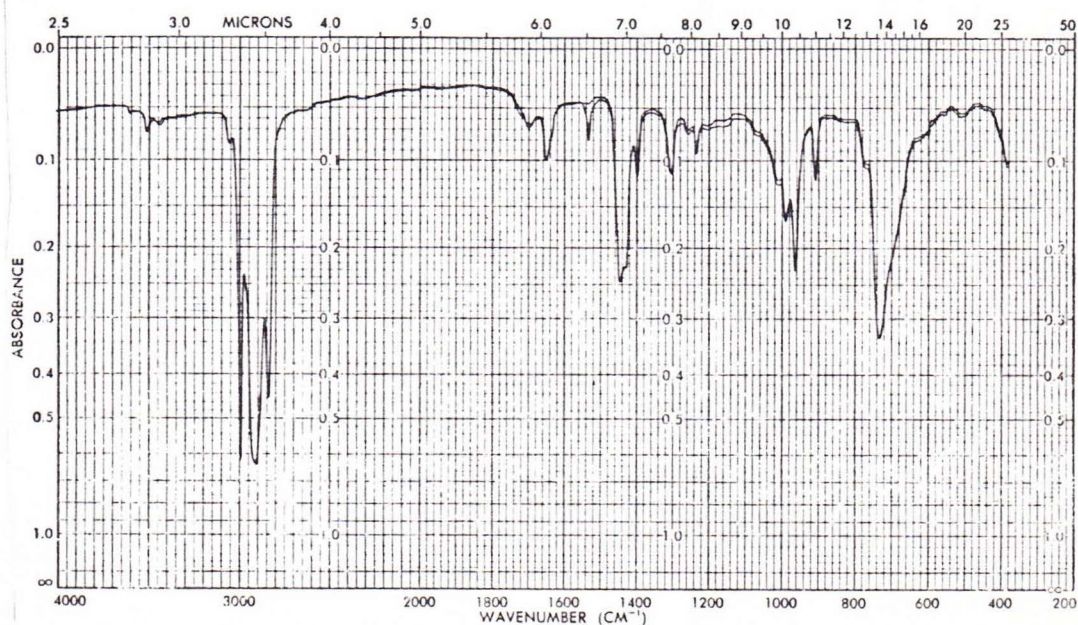


Plate #27 - 96 hours in oxygen: A small decrease in base line is occurring periodically from 1390cm^{-1} to the end of the spectrum. The peak at 1535cm^{-1} is increasing.

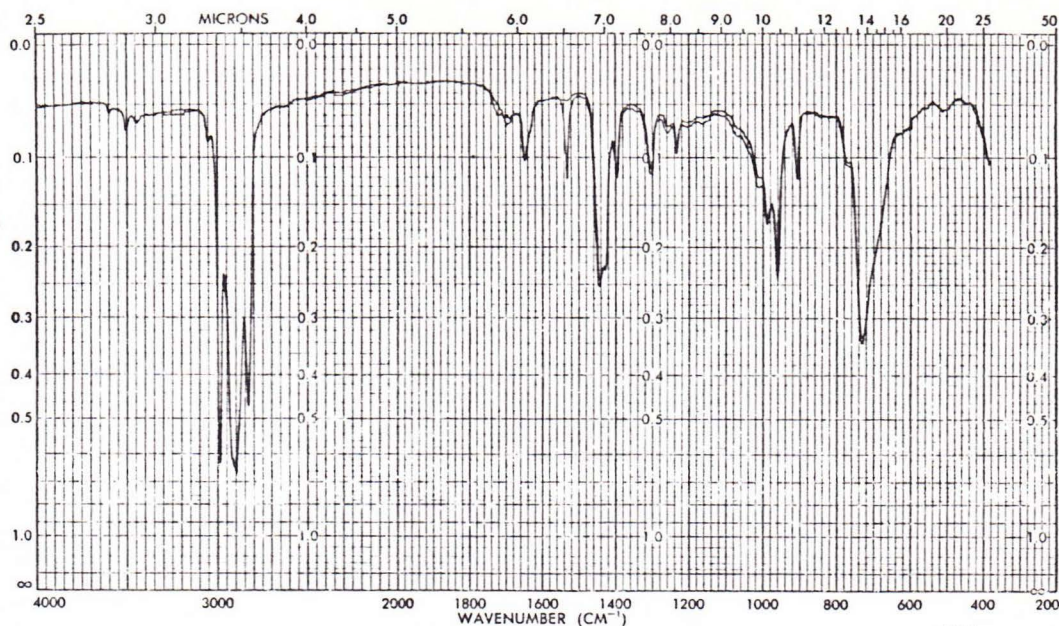


Plate #28 - 168 hrs. in oxygen: This spectrum is almost the same as the previous one with the exception of the increased absorption at 1535cm^{-1} .

DISCUSSION - POLYBUTADIENE RUBBER

As with natural rubber, the U.V. radiation and heat agings are non-distinguishable. However the new peak formed at 1365cm^{-1} for the ozone environment clearly separates this environment from the three other environmental conditions. Thus, as it is shown in Table V, one could distinguish between three causes of degradation; (1) oxygen, (2) ozone, and (3) heat or U.V. radiation.

CHLOROPRENE RUBBER - HEAT AGING 150°C - ASTM D573:

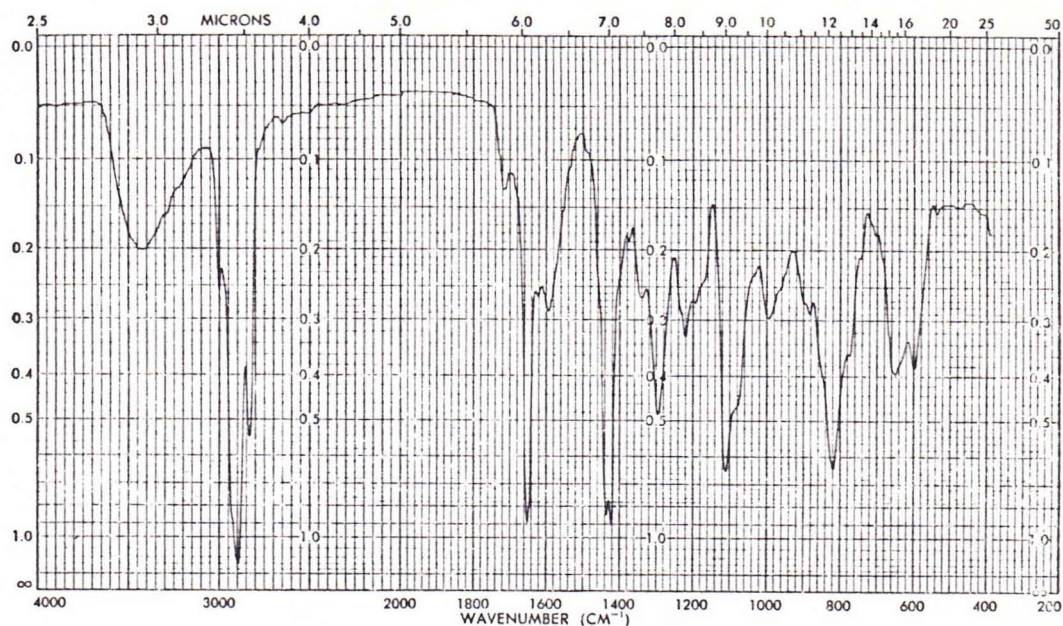


Plate #29 - CONTROL

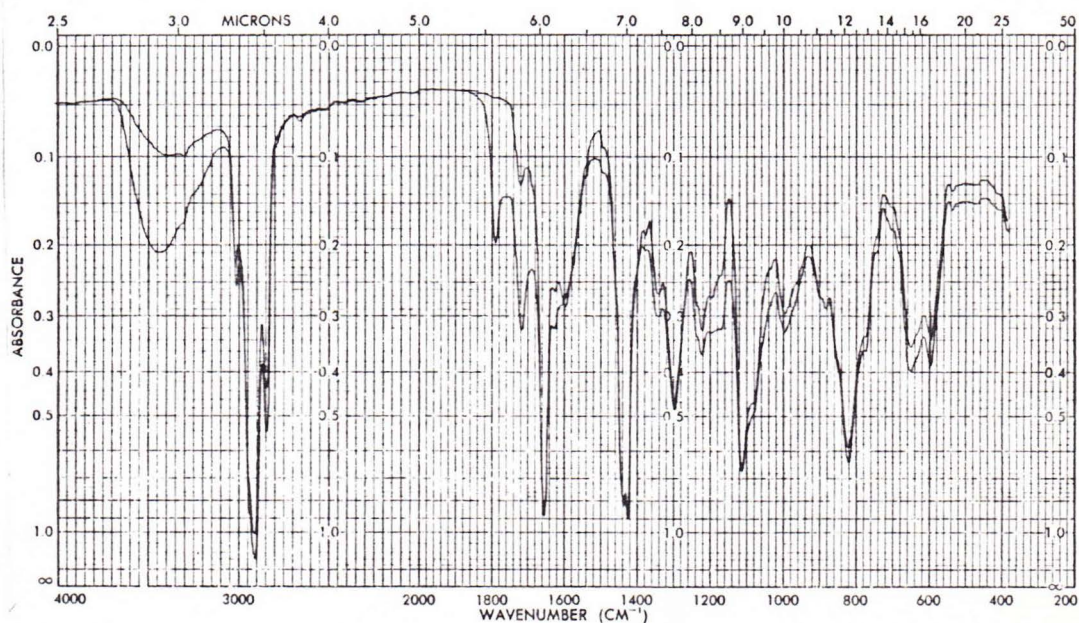


Plate #30 - 1 hr. at 150°C: There is a formation of new peak at 1790cm^{-1} but this occurred with all the different environmental agings. The peak at 1600cm^{-1} starts to disappear. Decreasing base line occurred from 1390cm^{-1} to 900cm^{-1} . From 900cm^{-1} to the end of the spectrum, the base line is higher than the control.

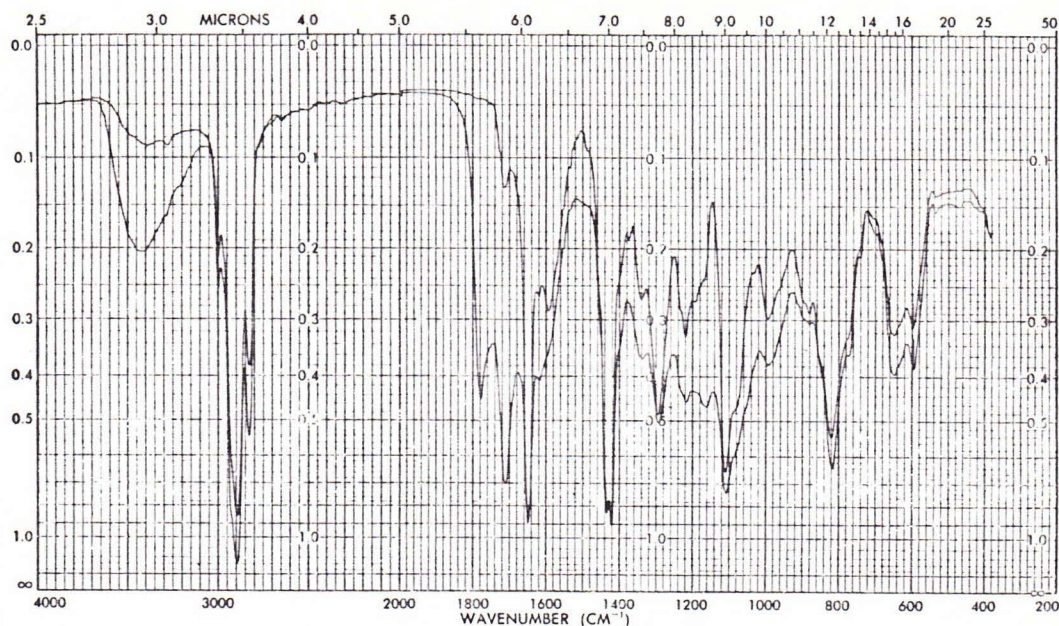


Plate #31 - Two hours at 150°C: A new peak formation at 1160cm^{-1} is the major difference between this spectra and the previous one. As well, the absorption from 1390cm^{-1} to 900cm^{-1} is greater. Again, from 900cm^{-1} to the end of the spectrum, the base line is higher than the control.

CHLOROPRENE RUBBER - OZONE, 40°C, 100 ppm, ASTM D1149

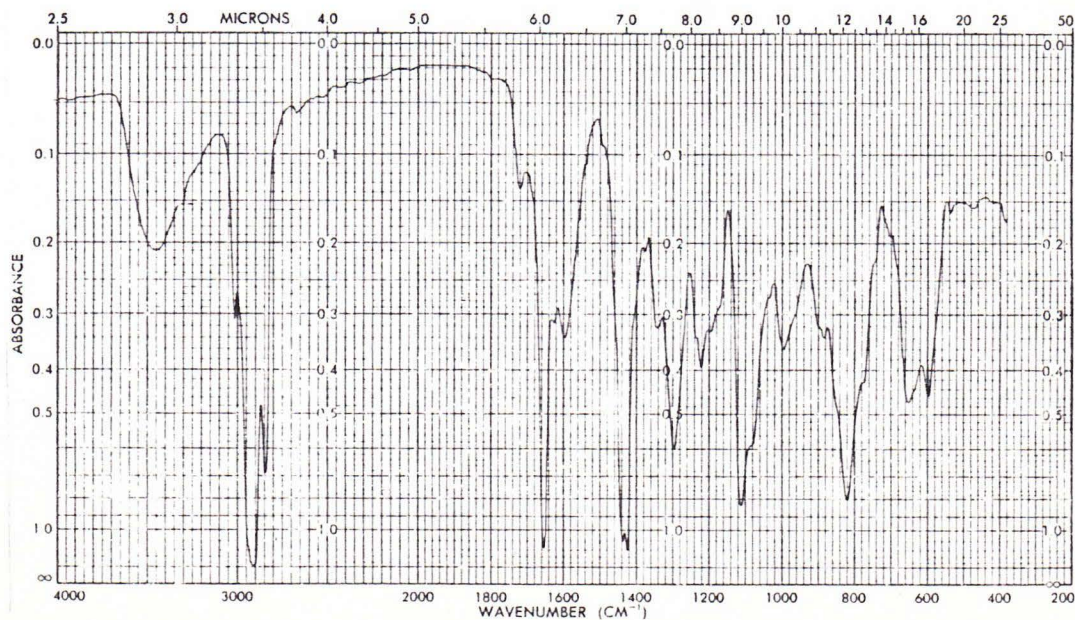


Plate #32 - CONTROL

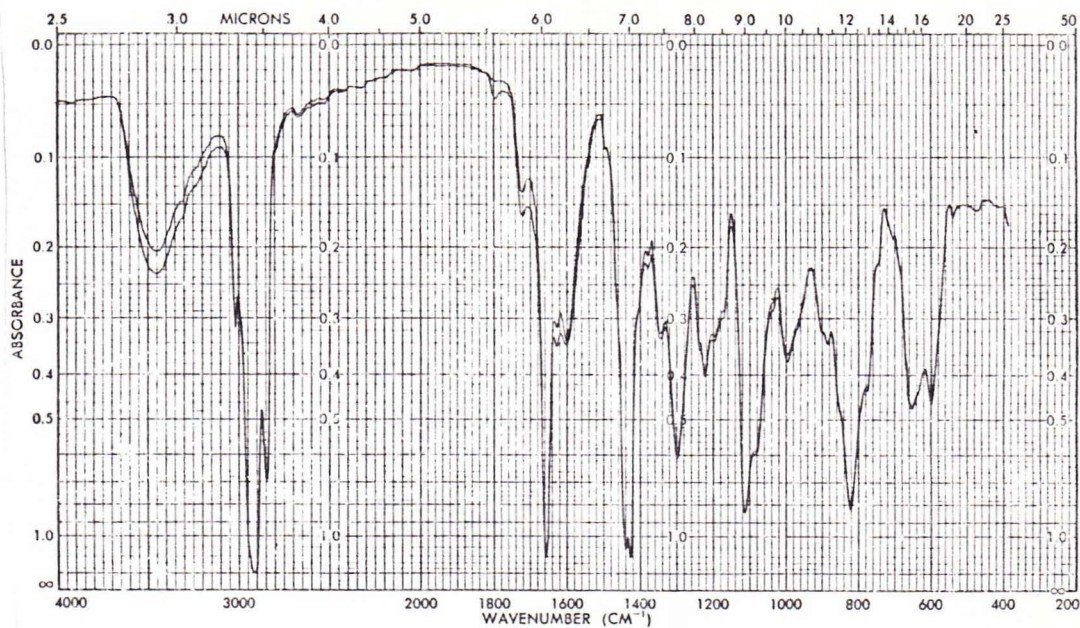


Plate #33 - 94 hours in ozone: With the exception of some lower base line activity, the spectrum is virtually unchanged.

CHLOROPRENE RUBBER - ULTRAVIOLET RADIATION, 40°C, ASTM D925

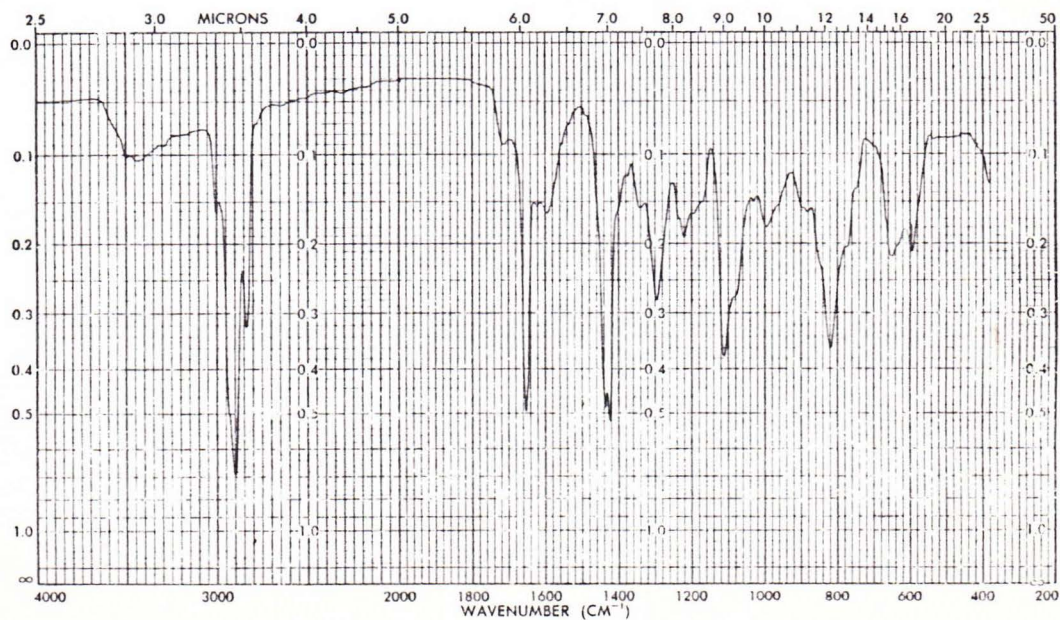


Plate #34 - CONTROL

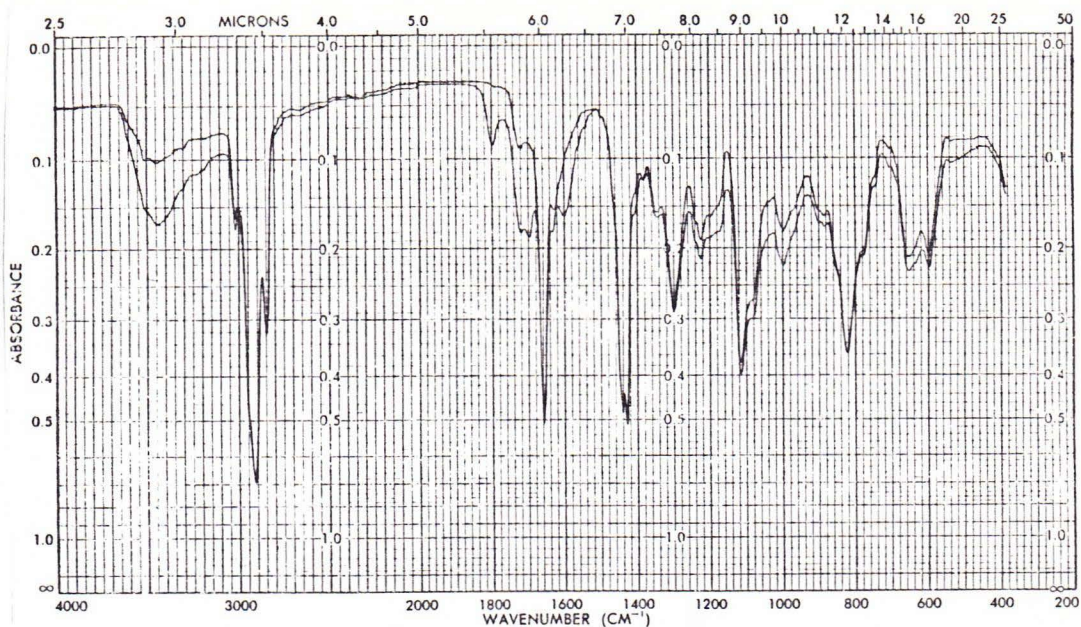


Plate #35 - 1 hour under U.V. radiation: New peaks occur at 1800cm^{-1} and 1700cm^{-1} . The base line has decreased in most places from 1420cm^{-1} throughout the rest of the spectra. In the heat aged spectrum the base line was higher than the control from 900cm^{-1} to the end of the spectrum.

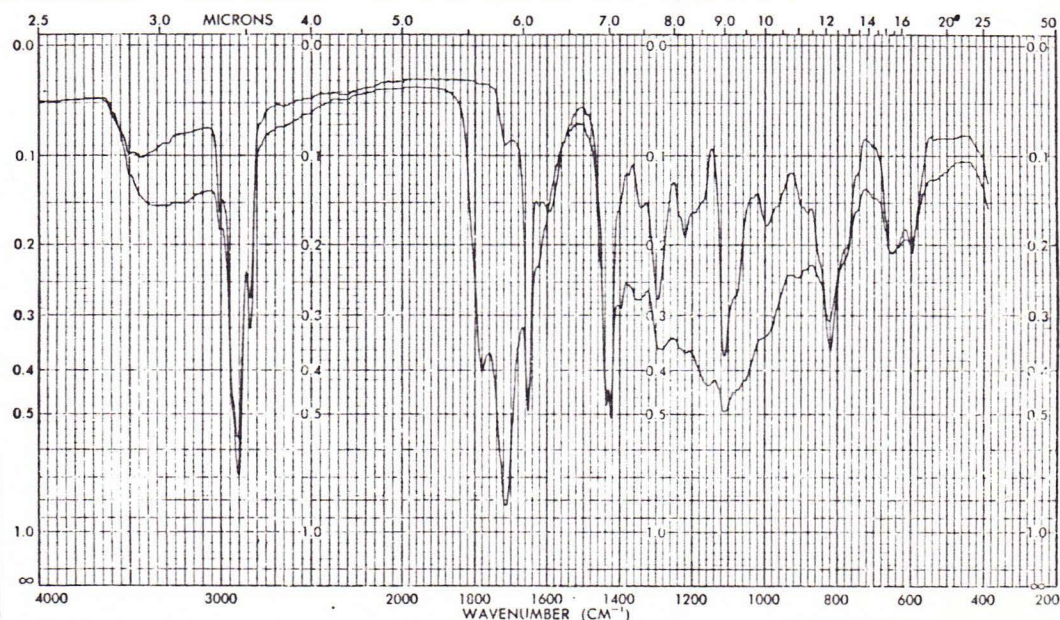


Plate #36 - 5 hours under U.V. radiation: A new peak occurs at 1160cm^{-1} as did the heat aged sample (plate #31). There is a small peak appearing at 910cm^{-1} making it possible to distinguish between the two methods of degradation by using thicker films.

CHLOROPRENE RUBBER - OXYGEN PRESSURE AGING, 2100kPa, 70°C, ASTM D532

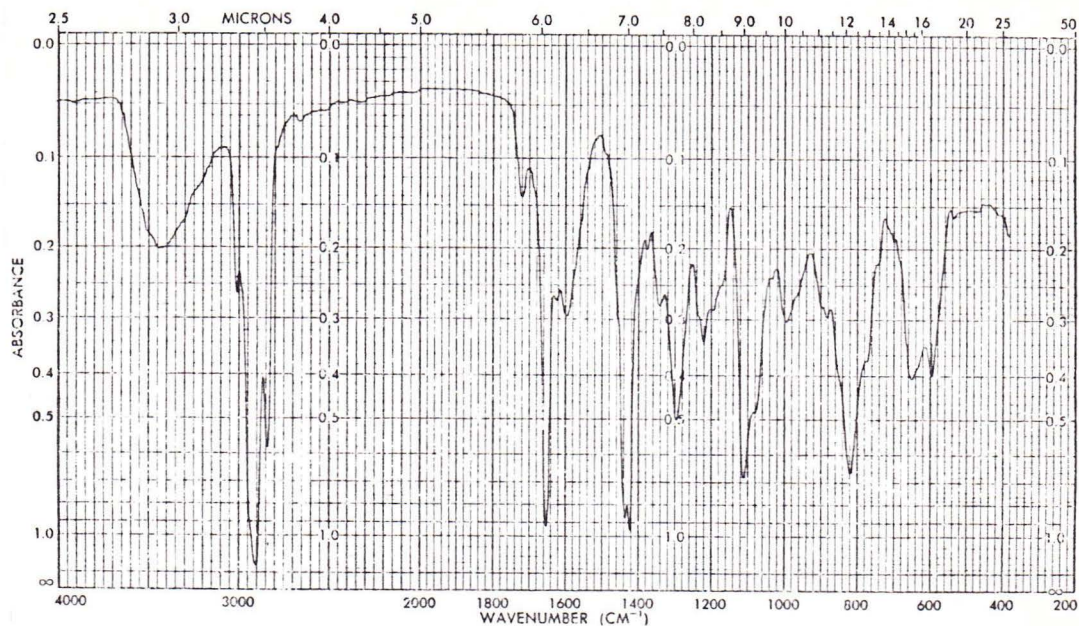


Plate #37 - CONTROL

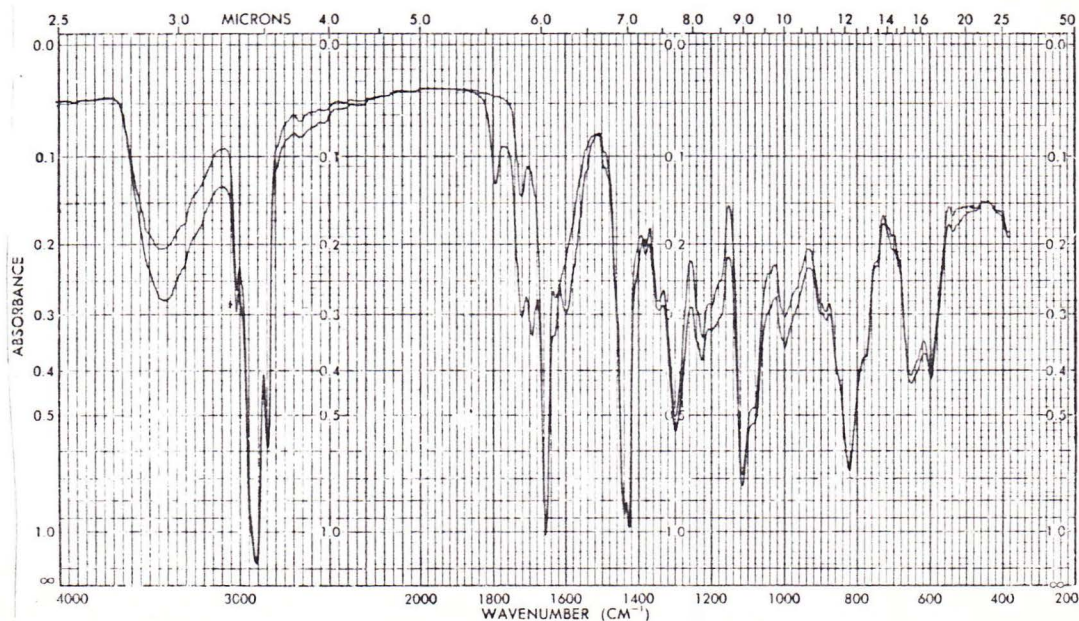


Plate #38 - 96 hours in oxygen: A distinguishing characteristic occurred with two peaks occurring at 1720cm^{-1} and 1695cm^{-1} . The base line decreases throughout the spectrum from 1410cm^{-1} .

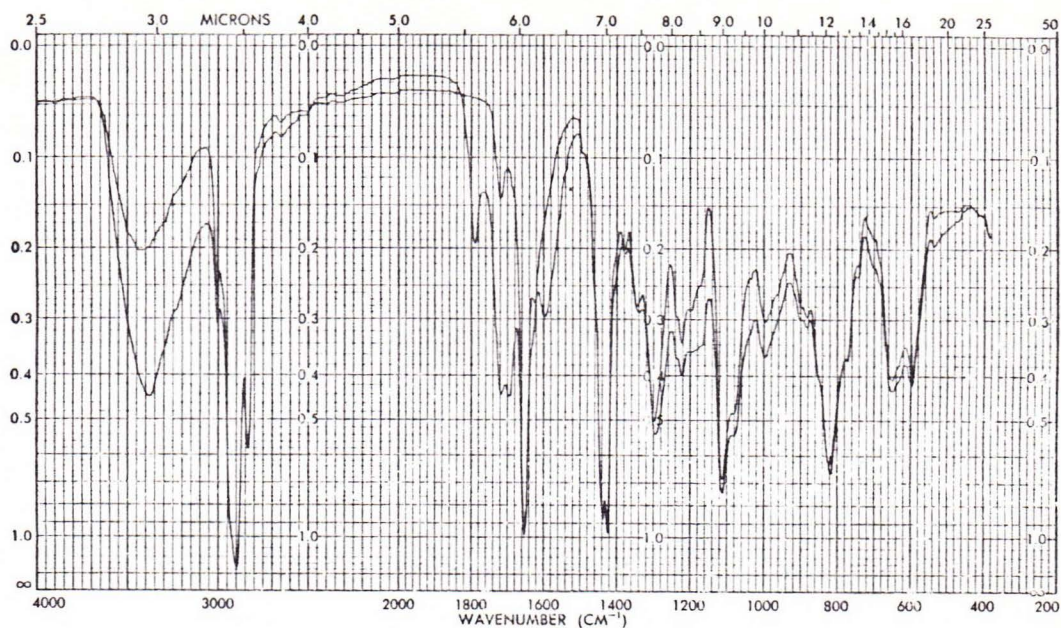


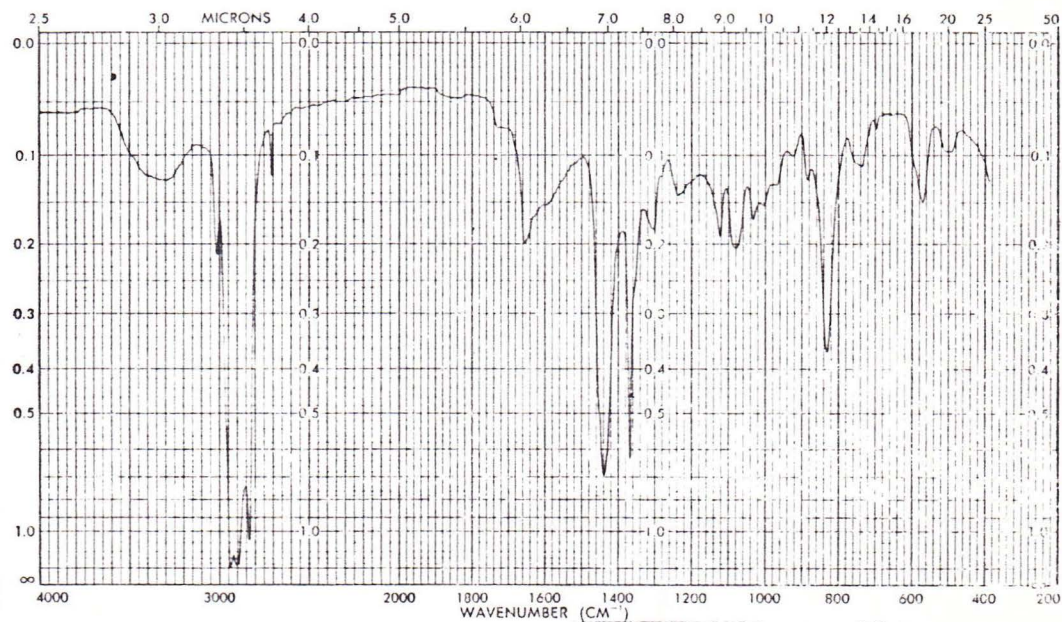
Plate #39 - 120 hr. in oxygen: Again the two peaks at 1720cm^{-1} and 1695cm^{-1} are present. Other than this the spectrum is similar to the previous one.

DISCUSSION - CHLOROPRENE RUBBER

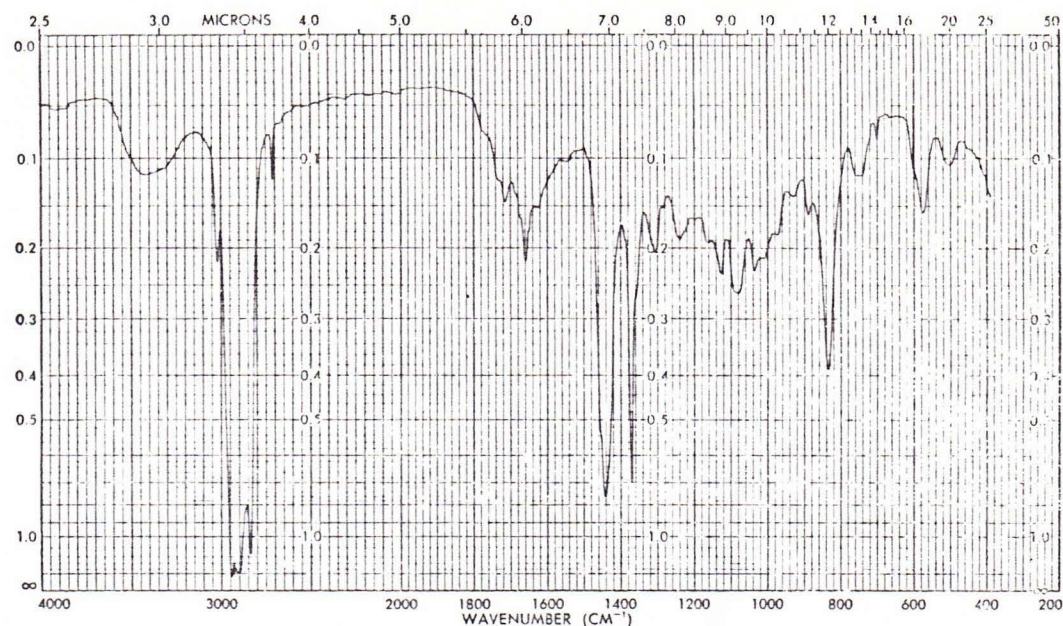
The oxygen aged sample of chloroprene rubber is most distinguished from the other modes of degradation. The ozone spectrum is distinguished from the other three environments by the absence of any change. Again, the heat aging and U.V. radiation are very similar with the exception of the increasing base line from 900cm^{-1} to 200cm^{-1} . Without making absorption measurements it would be difficult to distinguish between these two forms of degradation. Table VI will show the pertinent spectra changes that occur with chloroprene rubber.

AN EXAMPLE ENCOUNTERED IN THE FIELD

Many kinds of latex products exist which are produced from natural rubber. Two spectra are shown on one such product; spectrum A, which is the unaged product and spectrum B, which is the degraded product. In spectrum B, the peaks at 1160cm^{-1} and 1710cm^{-1} as previously shown, (plates #3 and #11), indicate either U.V. radiation or heat degradation. Knowing the history of the product may help to rule out one or the other since it was shown that infrared could not distinguish between these two modes of degradation. None the less, the information above helped to provide a solution to prevent the problem from reoccurring.



Spectrum A: Natural Rubber Control



Spectrum B: Degradated Natural Rubber

CONCLUSION

It has been shown that one can differentiate between some environmental causes of rubber degradation using infrared spectroscopy. Knowing the environment of a failed product may help the analyst rule out certain possibilities just as using different analytical tools may distinguish between environments that infrared failed to show. Further work in this area of Product Failure is needed, which may enable the rubber chemist to accurately and expediently determine the cause of failure by analytical means.

TABLE I

	<u>Parts by Weight</u>
SMR 5	100.0
Zinc Oxide	3.0
Sulfur	3.5
Stearic Acid	0.5
MBT	0.5

TABLE II

	<u>Parts by Weight</u>
Polybutadiene (cis1203)	100.0
Zinc Oxide	3.0
Sulfur	1.5
Stearic Acid	2.0
TBBS	0.9

TABLE III

	<u>Parts by Weight</u>
*Chloroprene Rubber	100.0
Stearic Acid	0.5
Magnesium Oxide	5.0
Zinc Oxide	5.0

*Neoprene W was used.

TABLE IV

NATURAL RUBBER - MAJOR CHANGES IN SPECTRA

<u>Condition</u>	<u>Loss of Absorption, cm⁻¹</u>	<u>Gain in Absorption, cm⁻¹</u>	<u>New Peaks, cm⁻¹</u>
heat	2900, 1440, 960	1710, 1660	1160
ozone			1530
U.V. radiation	2900, 1440, 960	1710, 1660	1160
oxygen			1530

TABLE V

POLYBUTADIENE RUBBER - MAJOR CHANGES IN SPECTRA

<u>Condition</u>	<u>Loss of Absorption, cm⁻¹</u>	<u>Gain in Absorption, cm⁻¹</u>	<u>New Peaks, cm⁻¹</u>
heat	2930	1720, 1695	1165, 1040
ozone		1710	1535, 1365
U.V. radiation	2930	1710, 1695	1535, 1165, 1040
oxygen			1535

TABLE VI

CHLOROPRENE RUBBER - MAJOR CHANGES IN SPECTRA

<u>Condition</u>	<u>Loss of Absorption, cm⁻¹</u>	<u>Gain in Absorption, cm⁻¹</u>	<u>New Peaks, cm⁻¹</u>
heat	2900, 1600	1710	1790, 1160
ozone		1720	1800
U.V. radiation	2900, 1600	1710	1790, 1160, 910
oxygen	1600	1720	1790, 1695

REFERENCES

1. J. B. Putman, C. R. Samples, and T. M. Knowles, "Systematic Analysis of Rubber Compounds," presented to the 116th Meeting of the ACS, Rubber Division, October, 1979.
2. Annual Book of ASTM Standards, Volume 37 (1981).

ACKNOWLEDGMENT

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