

HNBR and Long Term Serviceability in Modern Automotive Lubricants

Part - I : Analytical Study

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ABSTRACT

Hydrogenated nitrile (HNBR) elastomers are currently gaining interest for sealing applications because of their superior resistance to nucleophilic attack relative to nitriles and lower cost than fluoroelastomers. Long term immersion studies have shown that after prolonged exposure, i.e., over 1000 hours, at 150° C in automatic transmission fluids, HNBR elastomers show a sharp increase in hardness. This event occurs within a short period of time between 1500 to 2000 hours. Up to 1000 hours, these elastomers show good chemical resistance exhibiting only a slight change in hardness.

The objective of our study was to identify the primary mechanism which is responsible for such a dramatic increase in hardness. The changes in the chemistry of the elastomer were extensively studied using Fourier Transform Infrared Spectroscopy (FTIR). We have discovered that the increase in hardness is primarily due to chemical attack at the acrylonitrile sites. We have also discovered that this chemical attack first results in the formation of isocyanide or isonitrile ions. We have proposed a mechanism which involves crosslinking at the acrylonitrile sites through the formation of the isonitrile ions and subsequently forming an imide. The isonitrile intermediate forms ionic bonds resulting in the formation of an ionomer once the concentration becomes sufficiently high. Ultimately, these ions crosslink to form imides in the presence of oxygen or water. We believe that the formation of the ionomer and subsequently the imide is responsible for the increase in hardness.

To our knowledge, this is the first study to discover the formation of an isonitrile ionomer and conversion of HNBR into an imide in a basic lubricant environment.

INTRODUCTION

The evaluation and use of Hydrogenated Nitrile Butadiene Rubber (HNBR) has increased consistently over the past decade. HNBR has made significant in-roads into the On and Off - Highway vehicular markets. Several of our customers on various occasions have specifically requested the evaluation of HNBR in targeted applications.

Some proposed marketed advantages by the manufacturers of HNBR are: the superior high temperature performance, abrasion resistance, and chemical resistance compared to Nitrile (NBR); superior low temperature performance and toughness compared to Fluorocarbon (FKM); and better resistance to amine containing additive packages compared to vinylidene fluoride (VF₂) containing FKMs.¹ All of the above statements have their scientific basis, however the scope of this paper will focus on the chemical resistance of HNBR in lubricant additive packages.

Since the inception of HNBR, there has been the unofficial hypothesis that HNBR is not readily susceptible to degradation by nucleophilic or base containing additive packages, the way NBR's and VF₂ containing FKM's are degraded. There is no documented data describing the susceptibility of HNBR to such degradation. The discovery of this potential occurrence was made

five to six years ago by more than one company (part manufacturers and polymer manufacturers) when conducting long term immersion testing (> 1000 hours) in power steering and automotive transmission fluids. The HNBR would display only minimal changes, if any, from the start of test to 1000 hours. Then between 1000 and 2000 hours, the material would undergo a rapid hardening and / or a substantial change in physical properties. Inquiries made to the polymer manufacturers as to the cause and mechanism of this reaction or progression of reactions, yielded no plausible hypothesis or explanation. This lack of information and requests from our customers to evaluate the potential and performance of HNBR in specific applications, forced us to initiate a thorough investigation of this chemical reaction or reactions.

Literature searches showed that there have been numerous investigations and published reports documenting the performance of NBR and HNBR in electrophilic, hydrolytic, nucleophilic, and free-radical environments.²⁻⁷ All of this work except for Fath, Fahmy, and Scinto (1991) and Hertz, Bussem, and Farinella (1997) focused on the attack of NBR and HNBR in oilfield type environments. Fath, Fahmy, and Scinto compared the effect of Hypoid Gear lubricants containing conventional and thermally stable additives on NBR, HNBR, polyacrylate (ACM), ethylene - acrylic (EAM), and VF₂ containing FKM, however their testing was only for a duration of 504 hours.⁸ Degradation of a 95% saturated HNBR was seen in this test time, but this was probably due to the remaining unsaturation in the backbone. Hertz, Bussem, and Farinella have conducted investigations of HNBR in inorganic and new organic acid inhibited coolant systems and found degradative effects.⁹ The scope of their research efforts centered around mechanical properties of o-rings in the aforementioned environments and not degradation mechanisms.

We initiated our own investigation after finding no thoroughly documented experimental procedure or hypothesis in the literature as to what is occurring in HNBR at extended agings. The objectives of our study include:

1. Present documented evidence of chemical degradation of HNBR in an automatic transmission fluid.
2. Investigate the chemical reactions involved in the degradation phenomenon.
3. Propose a hypothesis to explain the chemical degradation mechanism.

EXPERIMENTAL

To study the mechanism of chemical degradation of HNBR, we formulated a special compound without any fillers. Our main objective for doing this was to eliminate any filler-lubricant interaction in order to make the system simpler to study. By keeping the fillers out of the compound, we were able to keep the original hardness of the compound very low, which enabled us to monitor the hardness change better. In addition, since we used Fourier Transform Infrared (FTIR) spectroscopy as our main tool for chemical analysis, eliminating the fillers improved the signal-to-noise ratio for better spectral interpretation. Our objective of understanding the degradation mechanism in a fundamental level, was not compromised by excluding the fillers.

The composition of the experimental compound is shown in Table 1. The compositions are based on the recommendations of the polymer manufacturer for a seal compound with the exception of the filler. In the spirit of the study, we have chosen not to disclose the source of the polymer or the other ingredients.

After measurement of the original microhardness, specimens were aged in an automatic transmission fluid (ATF) for a prolonged length of time (up to 3000 hours) at 150 °C (302 °F). Samples were removed after 750, 1500, and 3000 hours for microhardness and volume swell measurements.

Table 1. Composition of the experimental compound

	PHR
HNBR Polymer	100
Inorganic Base	5
Antioxidant	4
Plasticizer	5
Curative (40% Active Peroxide)	6

A swell test was done in methyl ethyl ketone (MEK) to compare the crosslink density of the samples before and after various aging times. The test was done using samples completely immersed in MEK at 25 °C until equilibrium was reached. The amount of solvent absorbed gave a qualitative indication of the crosslink density. Lower amounts of solvent absorbed indicates higher crosslink density.

The chemical changes were studied primarily by using a FTIR spectrometer. Samples were prepared by pyrolyzing small amounts of the material and depositing on KRS-5 disks. Analysis was done in the transmittance mode at 2 wavenumber resolution. Happ-Genzel apodization and zero filling were used. The generated spectra were carefully analyzed to identify the chemical changes.

In addition to the compound studied, other formulations were also examined to establish or verify a hypothesis. They will be described at appropriate places in the paper.

RESULTS AND DISCUSSION

IMMERSION STUDIES

The change in microhardness of the compound with aging in the lubricant is shown in Fig. 1. Clearly, the hardness had no significant change until about 1500 hours of aging, thereafter it increased very sharply from 47 IRHD to 86 IRHD between 1500 and 3000 hours. The slight initial drop is normal as the rubber gets plasticized by oil absorption.

We would like to state here that hardening of the compound occurred in two different ATF formulations demonstrating that such a phenomenon is characteristic of the elastomer and not the lubricant.

Figure 2 shows the volume swell of the compound. After an initial volume swell of about 10% at 750 hours of aging, there is a gradual increase up to 3000 hours. The trend of volume swell change does not seem to have any relationship to the trend of hardness change. The fact that the hardness increased in spite of additional oil absorption, overwhelmingly supports the occurrence of a chemical attack of the compound by the lubricant.

From the microhardness data of Fig. 1, several conclusions can be drawn. In short term immersion tests, up to about 1500 hours in this case, HNBR compounds would show excellent resistance to chemical attack by the lubricants. However, in long term immersion tests, they would show great susceptibility to attack. This suggests that the useful life of HNBR may be quite well defined. It is conceivable that the life will also depend on the operating conditions, such as temperature history, lubricant chemistry, and state of stress.

Therefore, selection of HNBR for a particular application will critically depend on the type of application and the expected life of the part. If the life expectancy is long, careful evaluation of long term immersion data should be made. More importantly, accurate correlation of laboratory conditions to field conditions must be made. Unlike in most other types of elastomers where the

chemical attack is more gradual, the risk with HNBR is greater, if the laboratory data is not correctly correlated to application conditions. We shall not dwell too much on this as the service life prediction with HNBR is beyond the scope of this study. Instead, we shall focus our attention on the mechanism responsible for this chemical attack.

While discussing hardness change of an elastomer in a lubricant environment, the first thing that warrants investigation is change in crosslink density. We have stated before that a solvent swell test was used to qualitatively monitor the change in crosslink density. The MEK swell data is shown in Fig 3. Note that the solvent swell decreases with an increase in crosslink density. Therefore, we can conclude from the data that, the increase in hardness of the compound at 3000 hours is a consequence of increase in the crosslink density.

One of the factors responsible for an increase in crosslink density is a crosslinking reaction at the residual unsaturation or other potential sites present in the compound after vulcanization. To verify if additional crosslinking at these sites would increase the hardness to a very high level, we formulated a compound with twice the curative level as the first compound, keeping everything else the same. After curing, there was a marginal increase in hardness, but nowhere near the increase in the hardness observed after 3000 hours of aging. This suggests that crosslinking across at the residual unsaturation or other potential sites alone cannot fully be responsible for the hardness increase. This leads us to investigate other possible factors.

The MEK swell of the new compound with twice the curative level is also shown in Fig. 3. The change in microhardness of this compound is shown in Fig. 4. The trend was repeated in this case as well.

Since neither the residual unsaturations nor other potential sites are primarily responsible for the hardness increase, we next focused our investigation on the role of the acrylonitrile (ACN) groups in the process. We created three different formulations by changing only the base polymer and keeping all other ingredients the same. The three polymers differed in their ACN content, which are 44%, 34% and 25%. All three compound were aged in the similar manner as before. The results obtained are quite interesting. The same trend, i.e., a sharp increase in microhardness, was observed for all the compounds. However, the time when the increase occurred reduced with an increase in the ACN content of the polymer. The compound with 44% ACN hardened the fastest followed by the 34% ACN compound. The 25% ACN compound stayed soft for the longest length of time. This shows that the ACN content has some relationship to the rate of hardening; the higher the ACN content, the faster is the hardening. This is another indication of the involvement of ACN groups in the hardening mechanism. This leads us to our chemical investigation of the mechanism primarily using the FTIR technique.

FTIR ANALYSIS

In our chemical investigation of the mechanism, we focused our analysis on two most plausible reactions -- crosslinking at the residual unsaturation or other potential sites and reaction of the acrylonitrile groups to form crosslinks.

FTIR scans of the compound before and after various aging times are shown in Fig. 6. As expected, the spectra show all the major peaks of hydrogenated nitrile. These include peaks at 2850 to 2950 cm^{-1} wavenumbers and 1460 cm^{-1} wavenumber corresponding to the CH_2 groups of hydrogenated butadiene, and a set of dual peaks at about 2220 and 2240 cm^{-1} wavenumbers corresponding to the $-\text{C}\equiv\text{N}$ groups. The spectra also contains some additional secondary peaks.

The regions of the spectra which relate to the $\text{C}=\text{C}$ groups, the unsaturation sites of partially hydrogenated butadiene which form the cure sites, are shown in an expanded form in Fig. 7. They are approximately at 3070 cm^{-1} and the 990 cm^{-1} wavenumbers. The presence of these groups in the original compound indicates the presence of some residual unsaturation sites. The reduction in the intensity of these peaks after aging would signify crosslinking at the residual

sites. However, it can be seen that there is little change in the intensity of these peaks after aging. This further supports the fact that residual unsaturations are not primarily responsible for the increase in the hardness of the compound. That no additional crosslinking took place in spite of the presence of excess cure sites, is possibly due to steric hindrance to such a reaction.

Next, the region of the spectra which relates to the acrylonitrile group is shown in an expanded form in Fig. 8. Some interesting observations can be made from a closer look at these peaks. First, the intensity of the acrylonitrile peaks at around 2220 and 2230 cm^{-1} wavenumbers did not change from the original as the material was aged up to 1500 hours. However, at 3000 hours, there was a significant reduction in the intensity of these peaks. Reduction of the intensity of these peaks is an indication of the consumption of acrylonitrile groups. Several reference spectra obtained from Nicolet FTIR Spectral Libraries of acrylonitrile:butadiene copolymers with various ACN contents are shown in Fig. 9. This fact provides further evidence for the involvement of acrylonitrile groups in the hardening mechanism.

Second, a new peak was observed at about 2160 cm^{-1} in two of the cases -- at 750 and 1500 hours of aging. This peak finally disappeared at 3000 hours. The appearance of this peak does not have a direct relationship to hardening of the compound, but the disappearance may have a link. This peak is attributed to isocyanide groups. A reference of an isocyanide peak from Nicolet FTIR Spectral Libraries is shown in Fig. 10. Isocyanides are ionic species with the structure $\text{C}\equiv\text{N}^+ -$. In this case, we speculate this to be isonitrile, which is the most plausible derivative of acrylonitrile. We believe that these isonitrile ionic species are formed from acrylonitrile groups in the lubricant environment. These ionic species could show strong interactions once the concentration of the species becomes sufficiently high, resulting in the formation of an ionomer. These ionic interactions act as pseudo-crosslinks.

To our knowledge, this is the first study to discover the formation of an isonitrile ionomer from acrylonitrile in the lubricant environment.

These isonitrile groups are not very stable. The disappearance of this peak at 3000 hours of aging may be a result of a reaction of these species.

Another area where significant change was observed is in the region of 1720 cm^{-1} wavenumber. This region is shown in the expanded form in Fig. 11. Up to 1500 hours of aging there was no change in the intensity of the peak, but at 3000 hours this peak was much increased in intensity. A peak at this frequency is attributed to aldehydes, esters, amides or imides. However, the simultaneous decrease in the acrylonitrile groups and the increase in the carbonyl groups suggest a conversion reaction of the acrylonitrile groups into amides or imides, and excludes any esterification reaction. Additionally, since amide groups show strong peaks at 3200 - 3400 cm^{-1} wavenumbers, the lack of these peaks in the spectra exclude the formation of amides. Therefore, we believe that imides are ultimately formed from the isonitrile ions. Imides could stoichiometrically form by a hydrolysis reaction by releasing NH_3 . At this time we do not have evidence to verify if ammonia is released.

From the structure of isonitrile, the conversion of isonitriles into imines appears to be more plausible. Although infrared peaks of imines and imides appear in the same general area, the peak in this case was much closer to an imide peak than an imine peak.

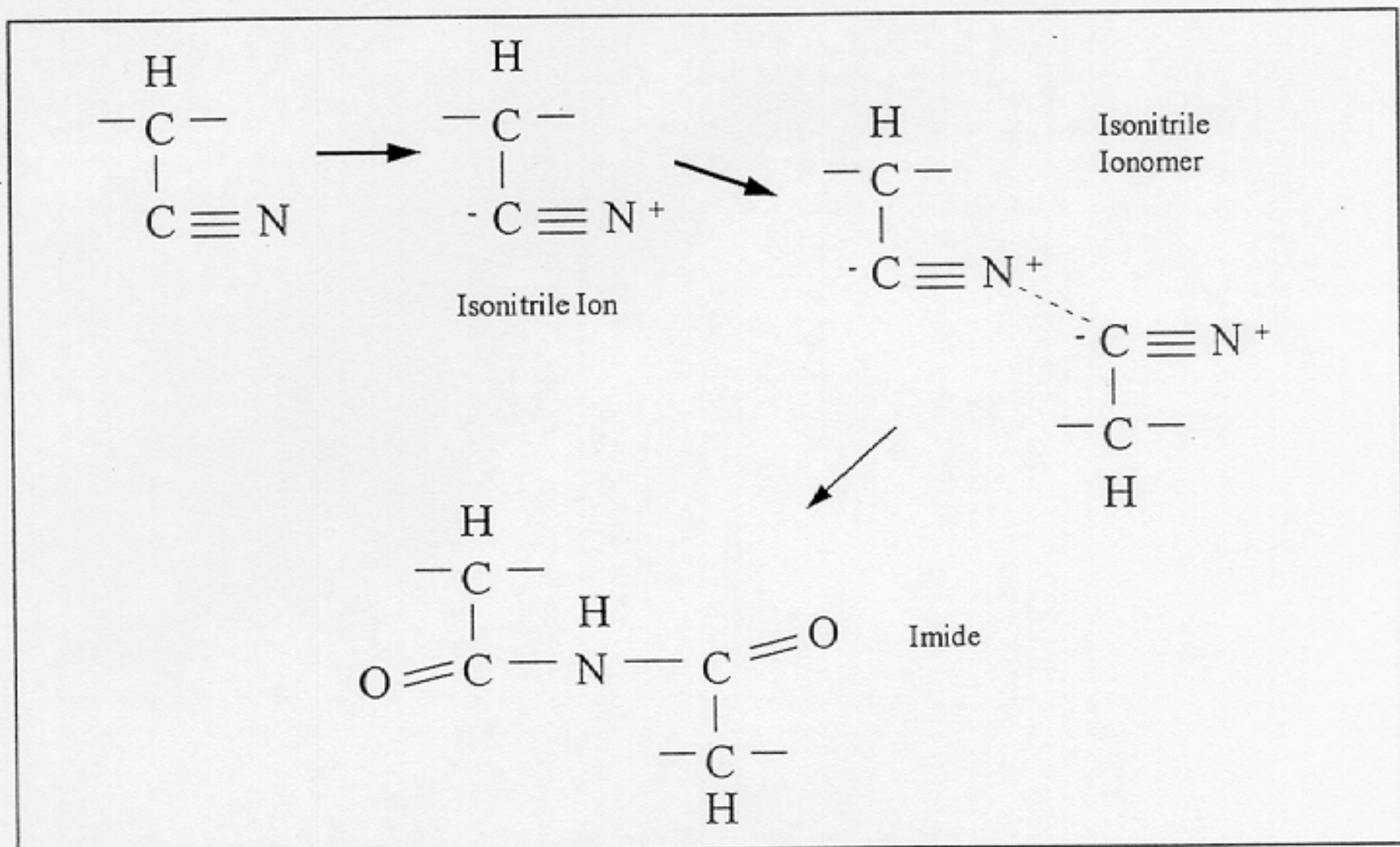
A PROPOSED MECHANISM

After analysis of all the data, we are proposing a hypothesis for the chemical degradation of HNBR in a lubricant environment. The steps involved are:

1. If stoichiometrically and sterically possible, residual unsaturations of the polymer will first crosslink through nucleophilic attack. However, this reaction can result in only a small increase in hardness.

2. The acrylonitrile groups are also chemically attacked which could result in a large increase in hardness. The chemical attack starts with the formation of isonitrile ions from acrylonitrile.
3. Once the ionic isonitriles are formed in sufficient quantities, strong ionic interaction occurs between the ions of adjacent molecules resulting in the formation of an ionomer. This can contribute to a substantial increase in hardness. There appears to be a critical concentration of the ionic species beyond which an ionomer is formed. We are speculating that the formation of the ionic species occurs as a step reaction.
4. As these ions are not very stable, they will ultimately crosslink covalently in presence of water to form imides. The formation of the imide structure can significantly contribute to the increase in hardness.

The proposed reaction scheme is shown below.



We would like to mention here that several questions still remain to be answered in our proposed mechanism. First, what initiates the formation of the isonitrile ionic species? Is it the nucleophiles in the lubricant or the electrophiles from lubricant oxidation products? Second, is there a specific additive in the lubricant which is responsible for this reaction? Although we have observed the hardening phenomenon in more than one lubricant, this will be a difficult question to answer because of our lack of knowledge of proprietary additive chemistry. Third, what is the contribution of the ionomer to the increase in hardness versus that from the formation of the imide?

Our work is still underway to answer some of these questions. Analysis using other techniques, such as Nuclear Magnetic Resonance (NMR), is also being done to validate our findings. The next part of our paper addresses the issue raised in the third question, in addition to providing valuable support to our proposed hypothesis.

CONCLUSIONS

1. We found that HNBR compounds undergo a sharp increase in their hardness in long term immersion tests in an automatic transmission fluid at elevated temperatures. The exact mechanism was investigated using FTIR spectroscopy.
2. Crosslinking at the residual unsaturations contribute marginally to the overall increase in hardness. The bulk of the increase is due to chemical attack of the acrylonitrile groups.
3. We have proposed a hypothesis where the chemical attack starts with the formation of isonitrile ionic species. Once the ionic concentration builds up to a sufficient level, an ionomer is formed through strong ionic interactions. These ionic interactions act as pseudo-crosslinks and help in increasing the hardness.
4. Ultimately, the ionomers convert to imides by addition of oxygen or water resulting in covalent bonds across the acrylonitrile groups. The formation of the ionomer and the imide results in the increase in hardness.

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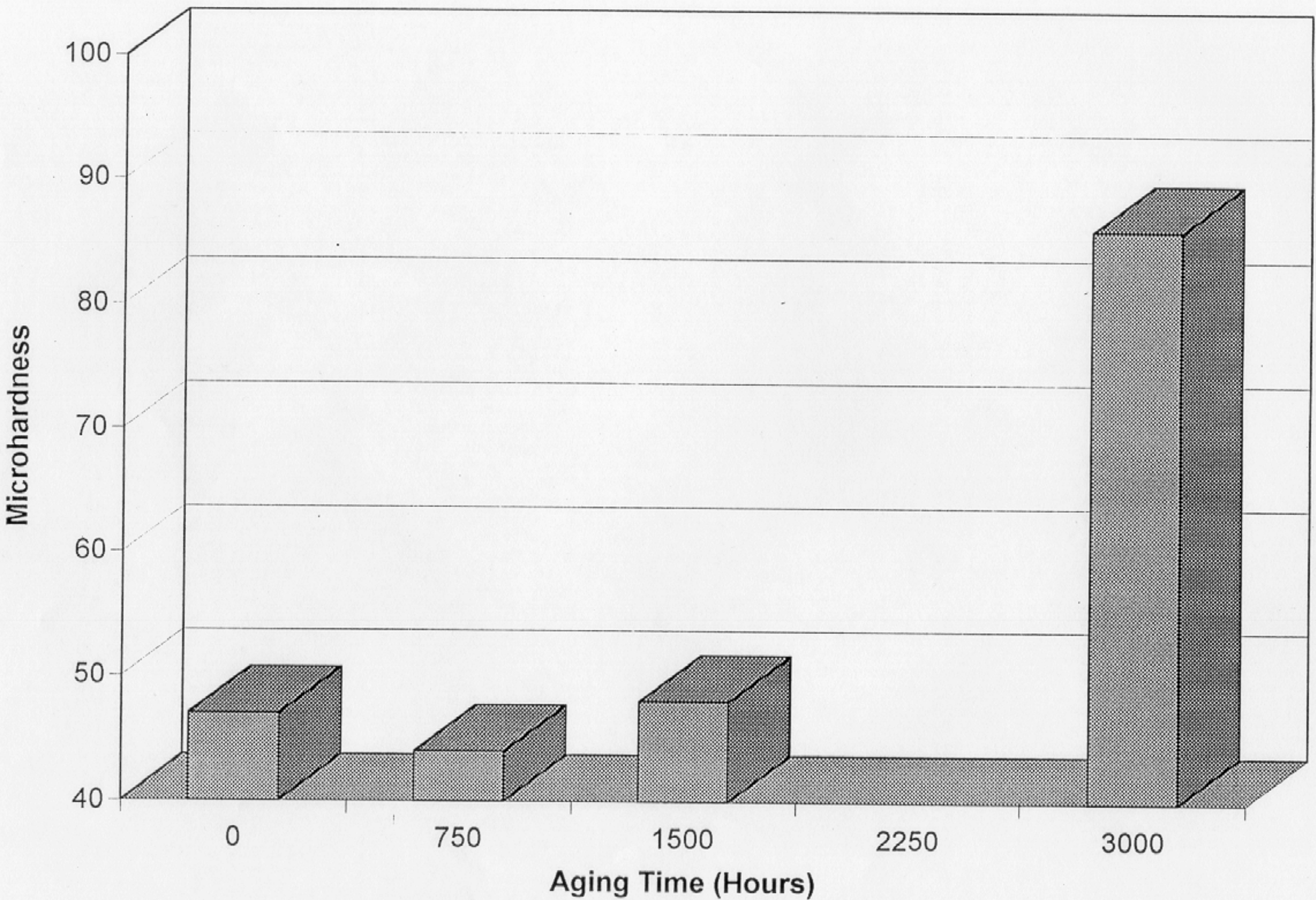


Fig. 1. Change in microhardness of the compound as a function of aging time

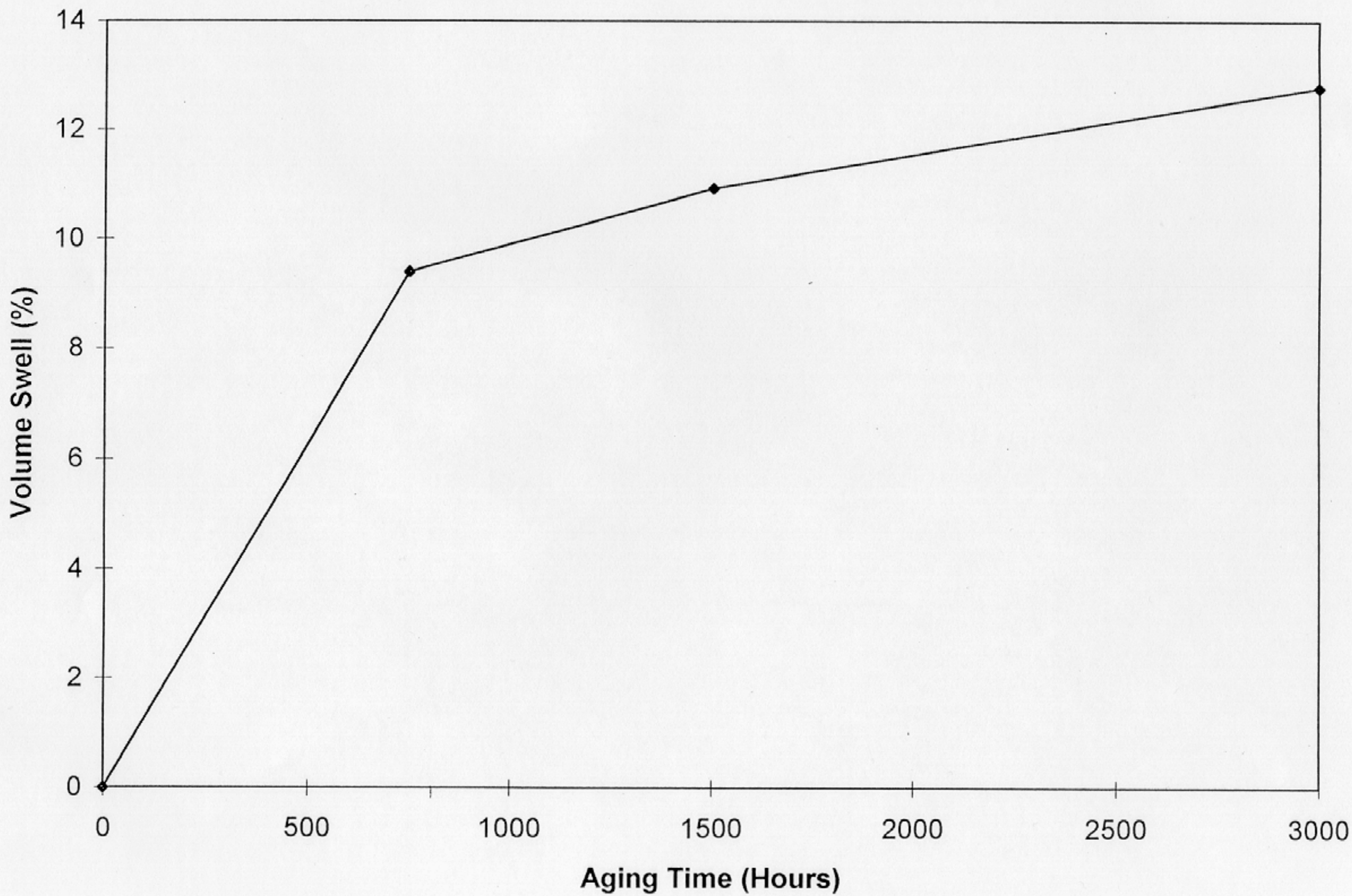


Fig. 2. Change in volume swell of the compound as a function of aging time

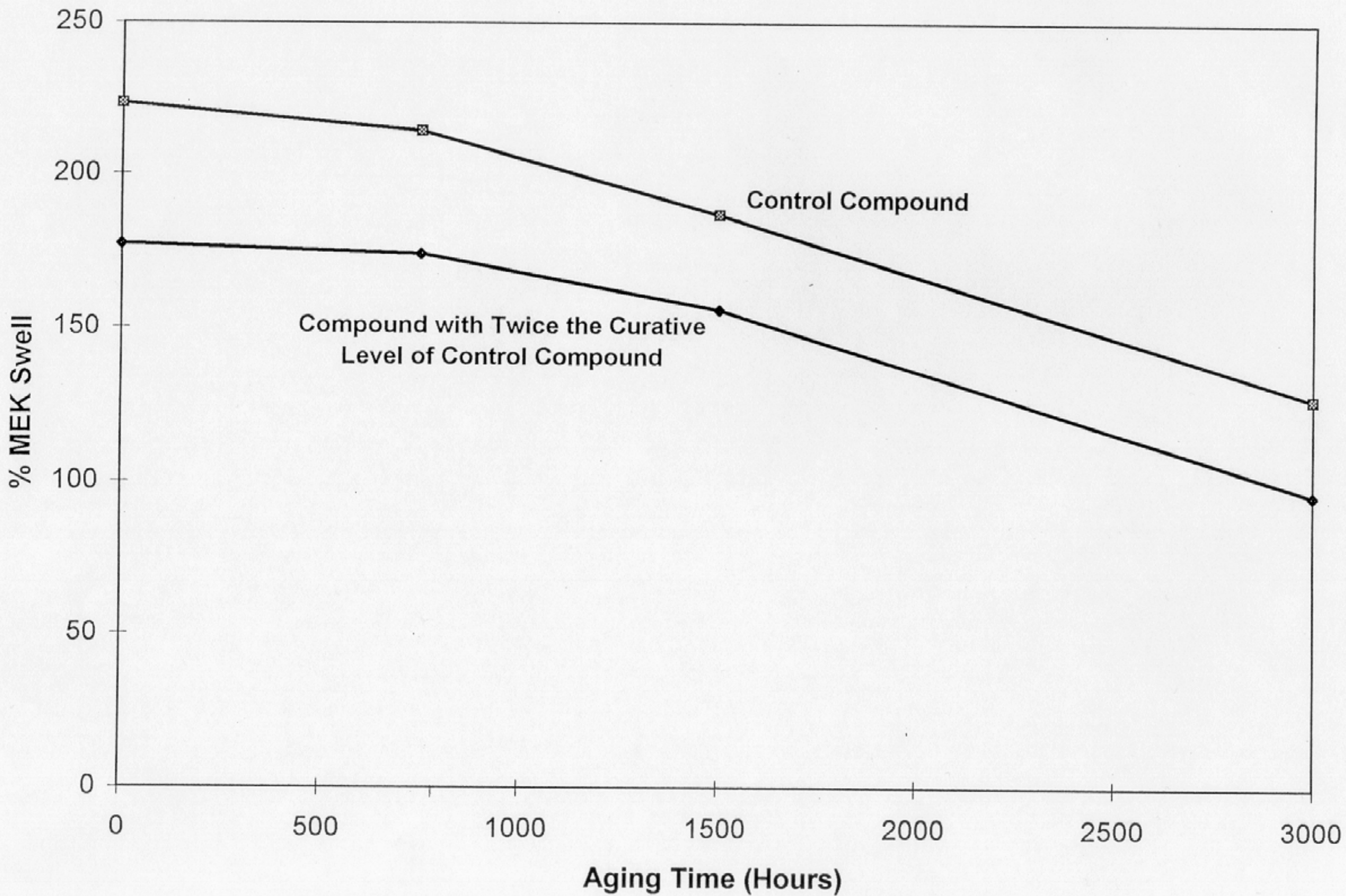


Fig. 3. Percent MEK swell (indicator of crosslink density) as a function of aging time

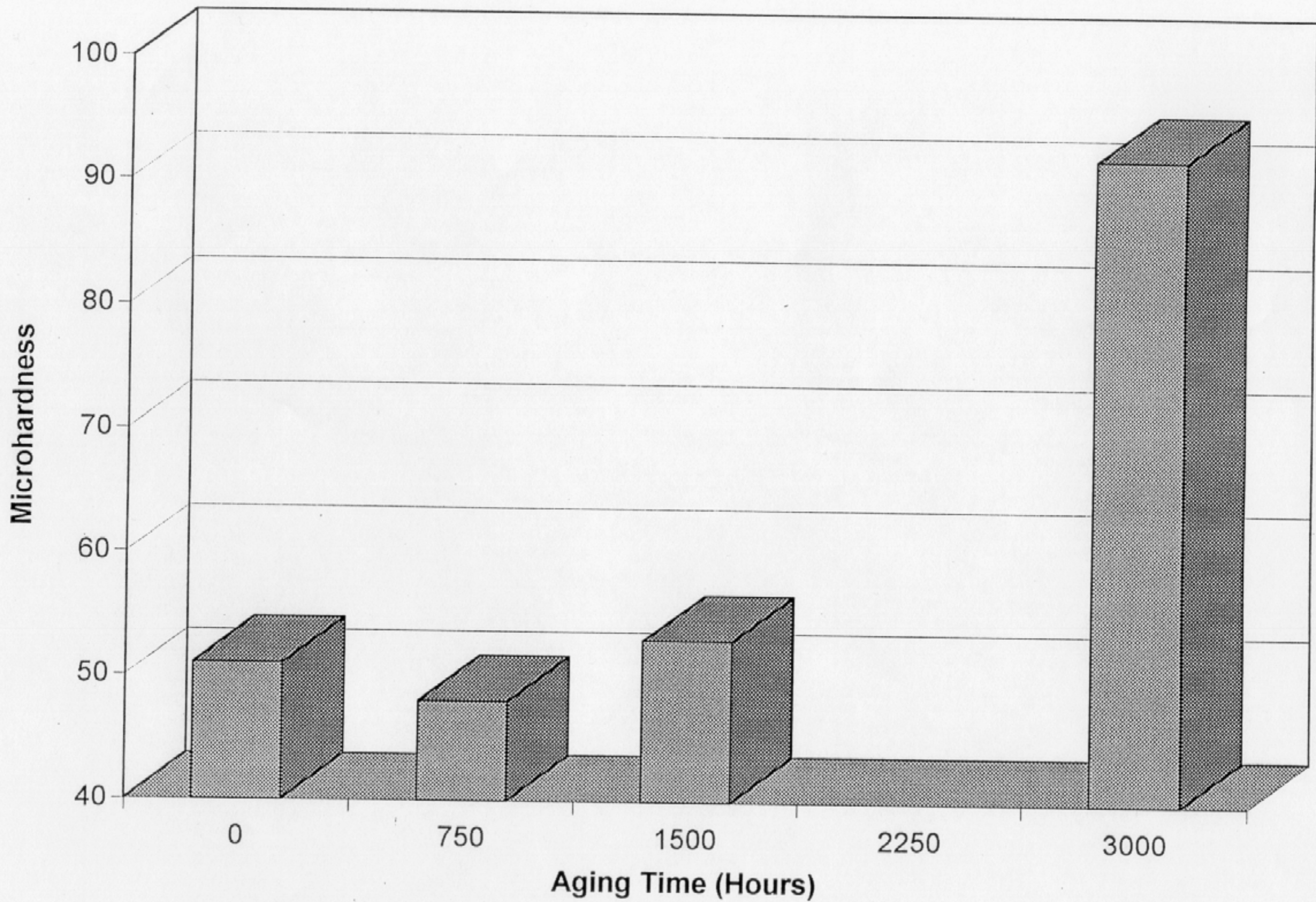


Fig. 4. Change in microhardness as a function of aging time

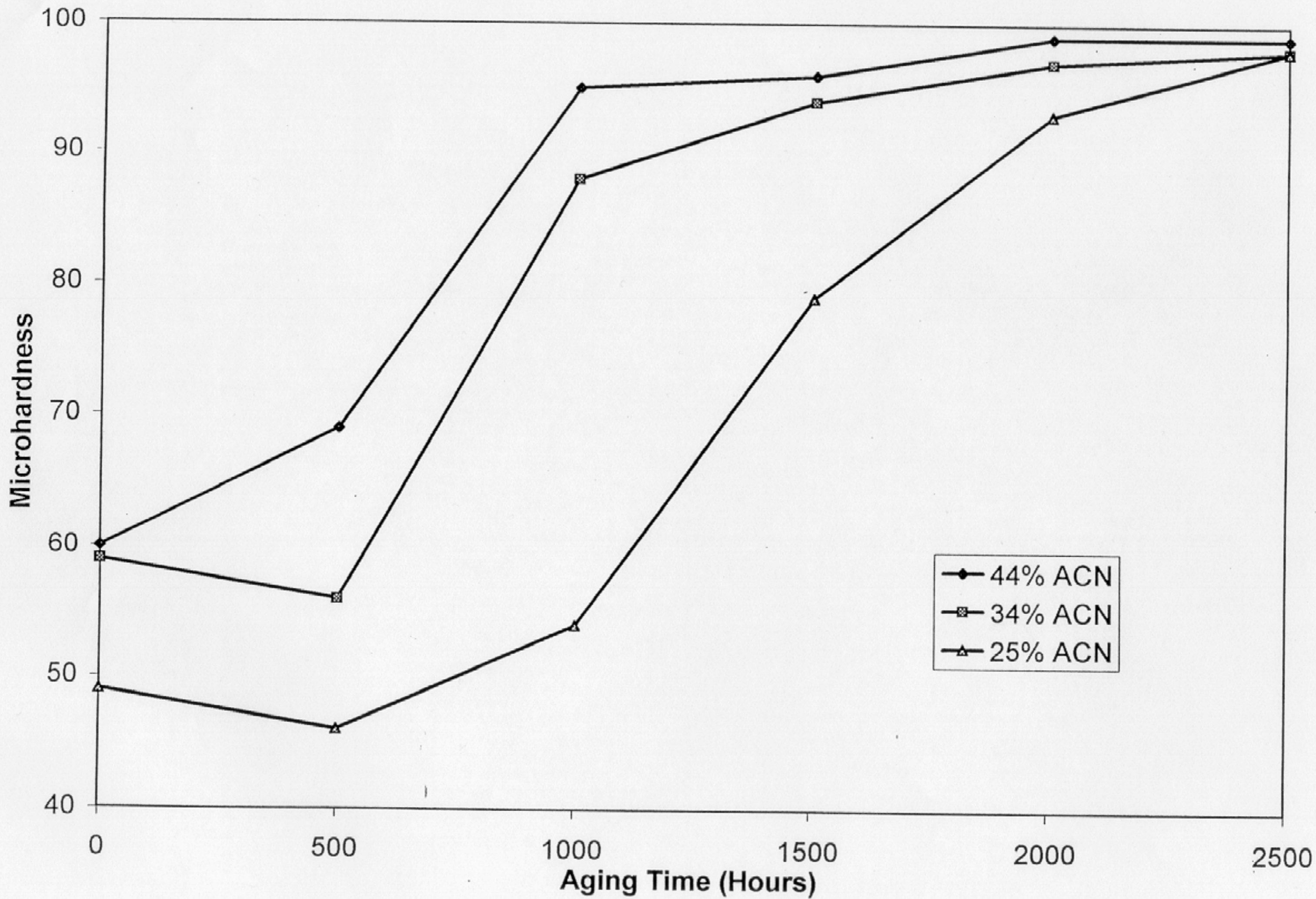


Fig. 5 Change in microhardness of the compounds with various ACN contents

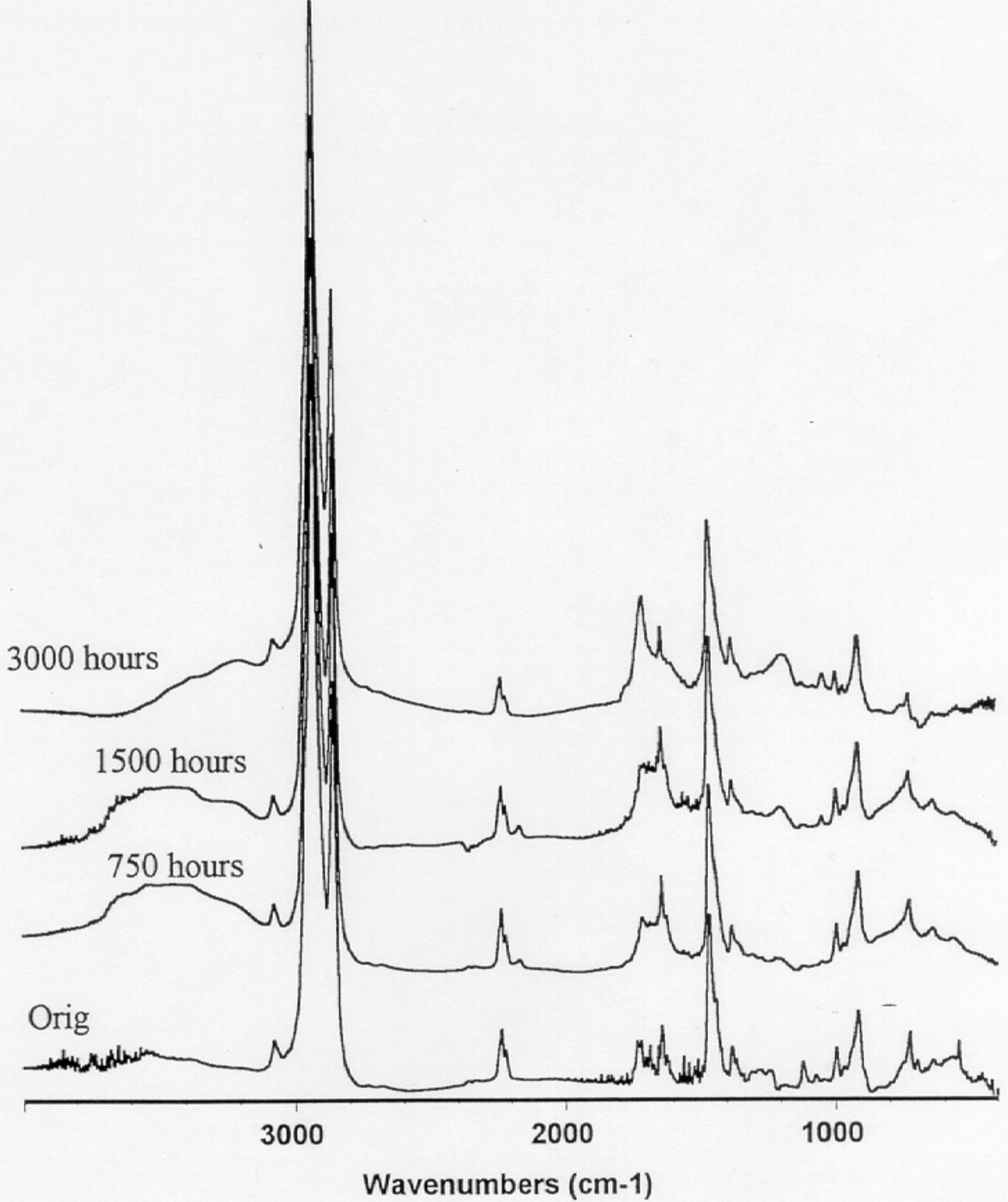


Fig. 6 FTIR spectra of the original and aged samples at various aging times

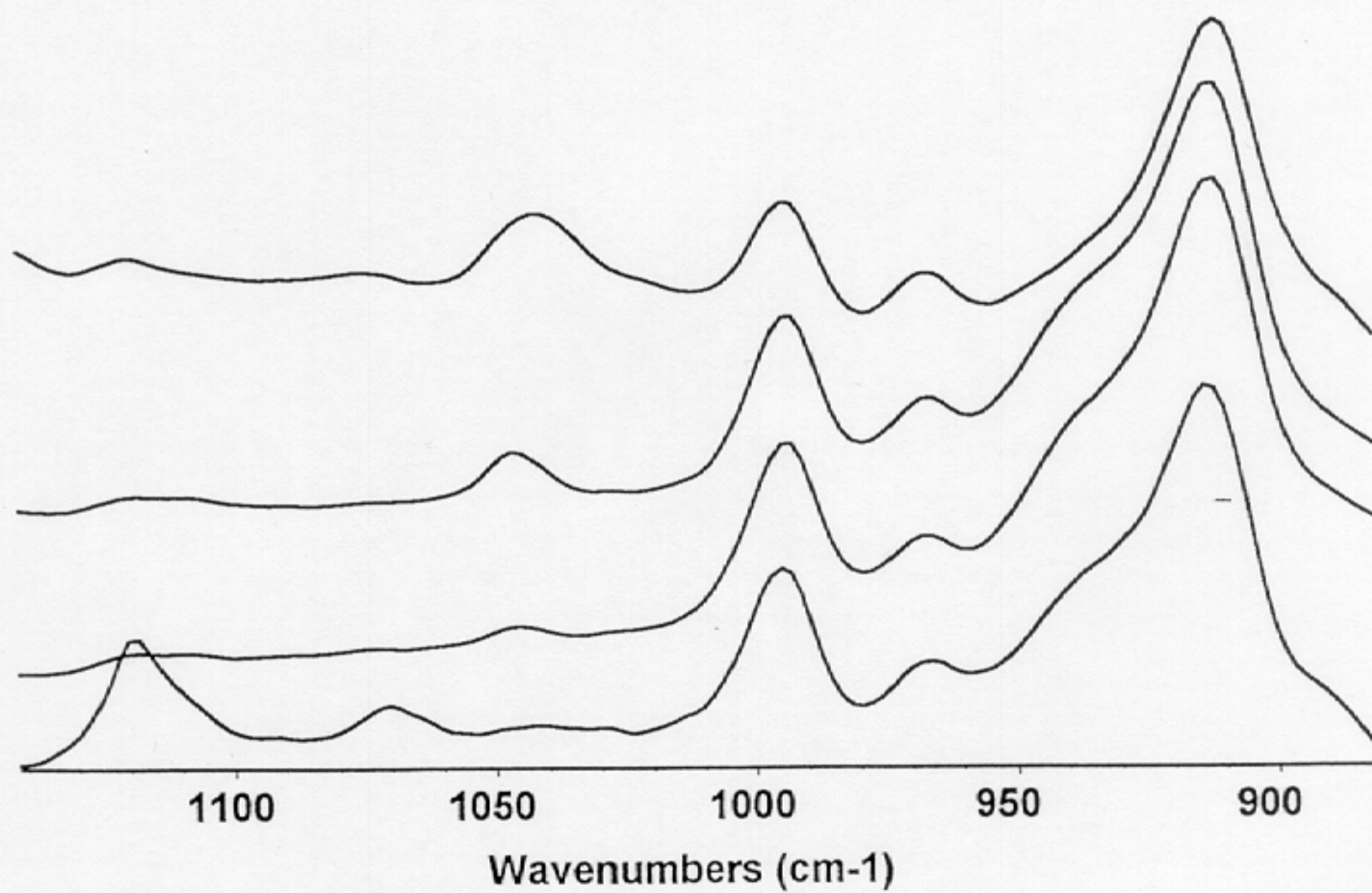
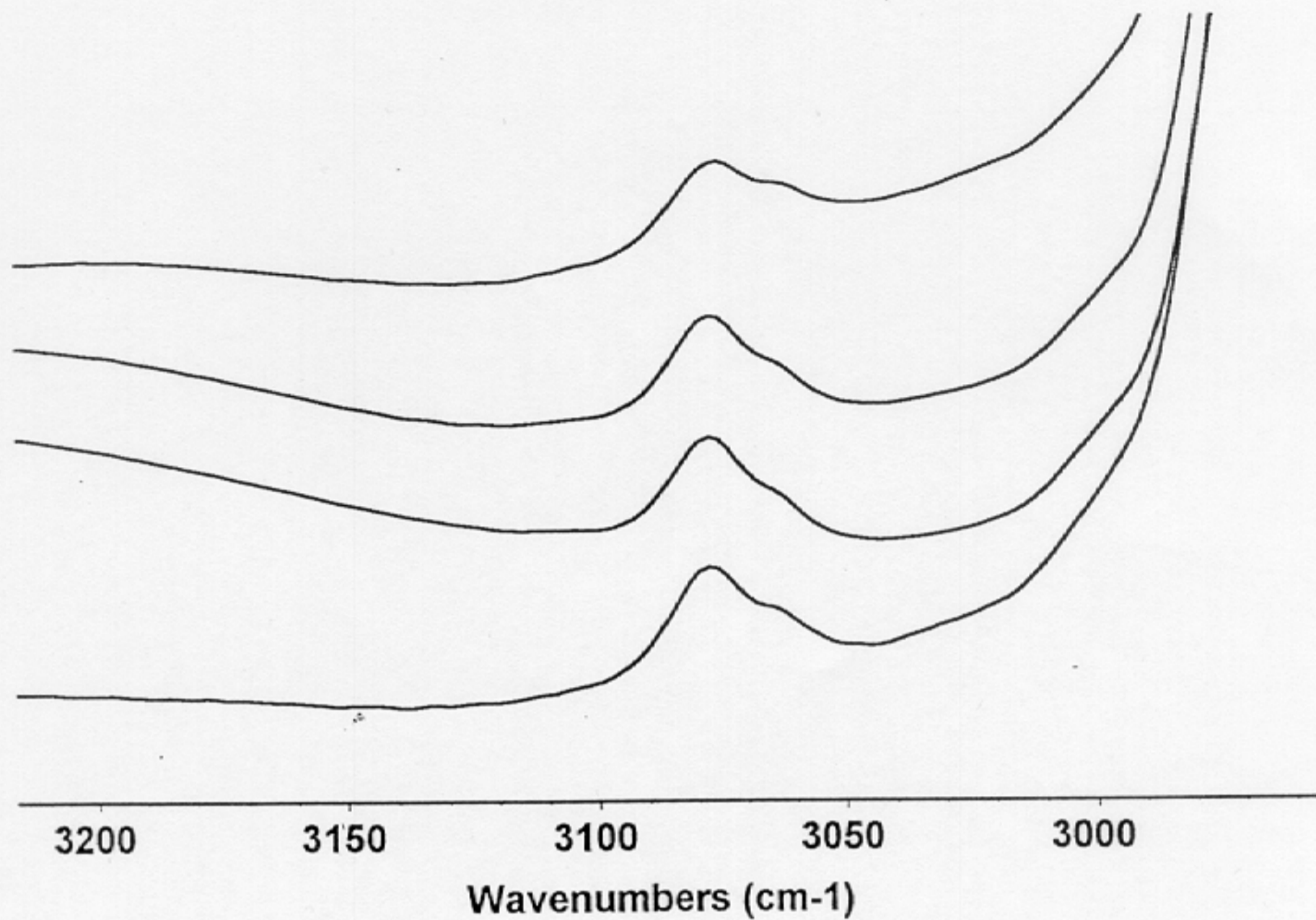


Fig. 7. Regions of the FTIR spectra attributed to the C=C group

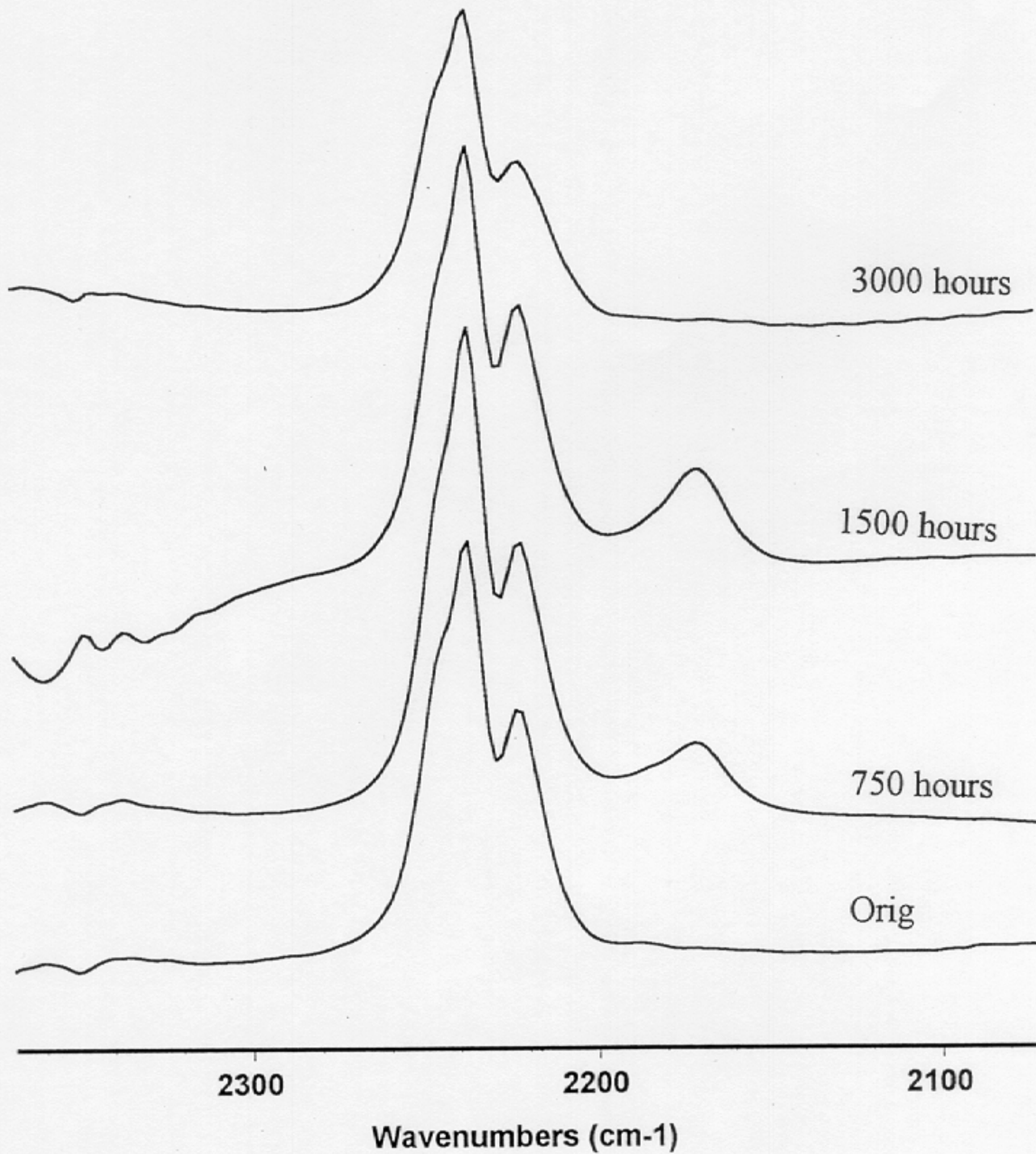


Fig. 8. Region of the FTIR spectra attributed to the C≡N group

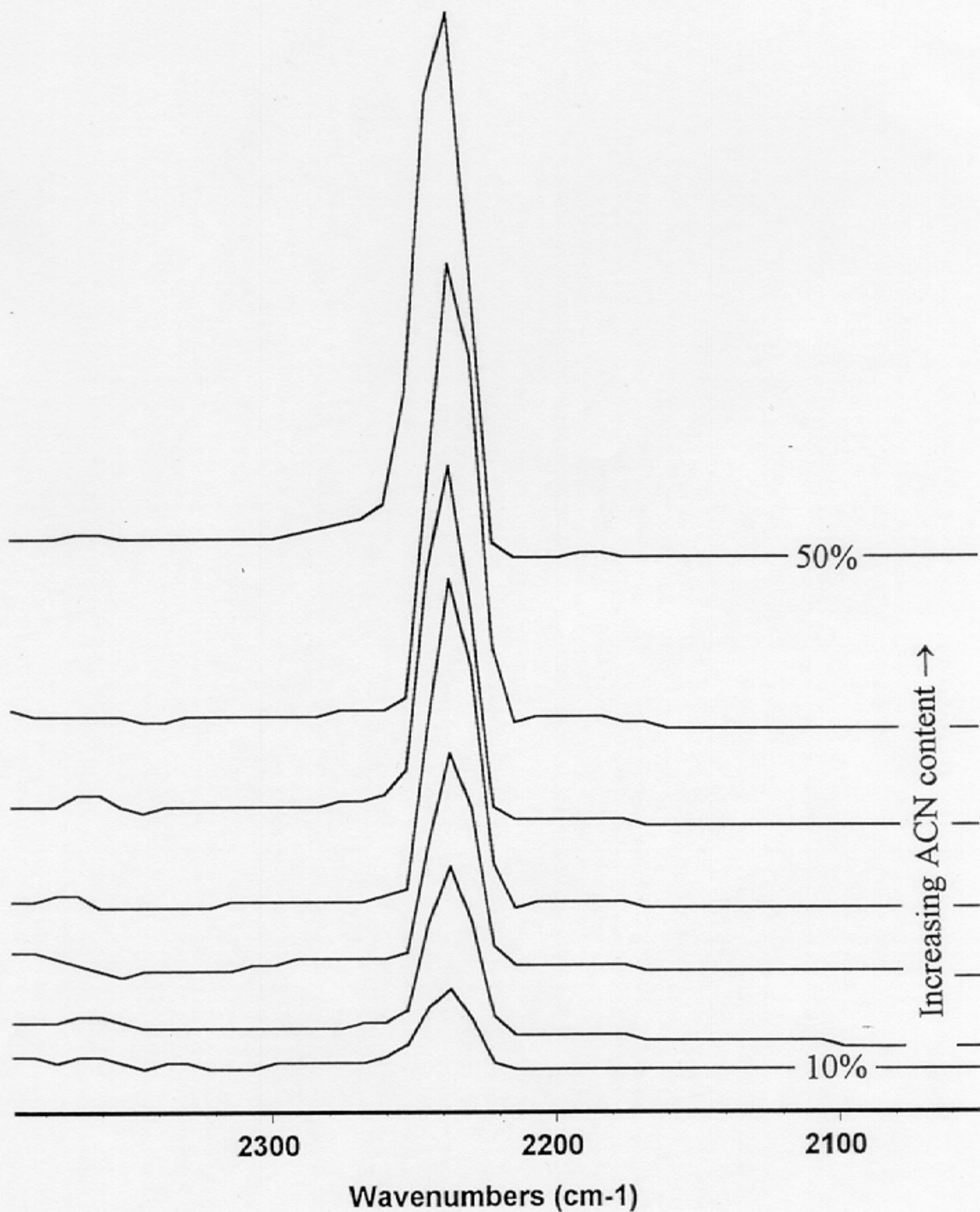


Fig. 9. ACN peak for compounds with various ACN contents (from Nicolet FTIR Spectral Libraries)

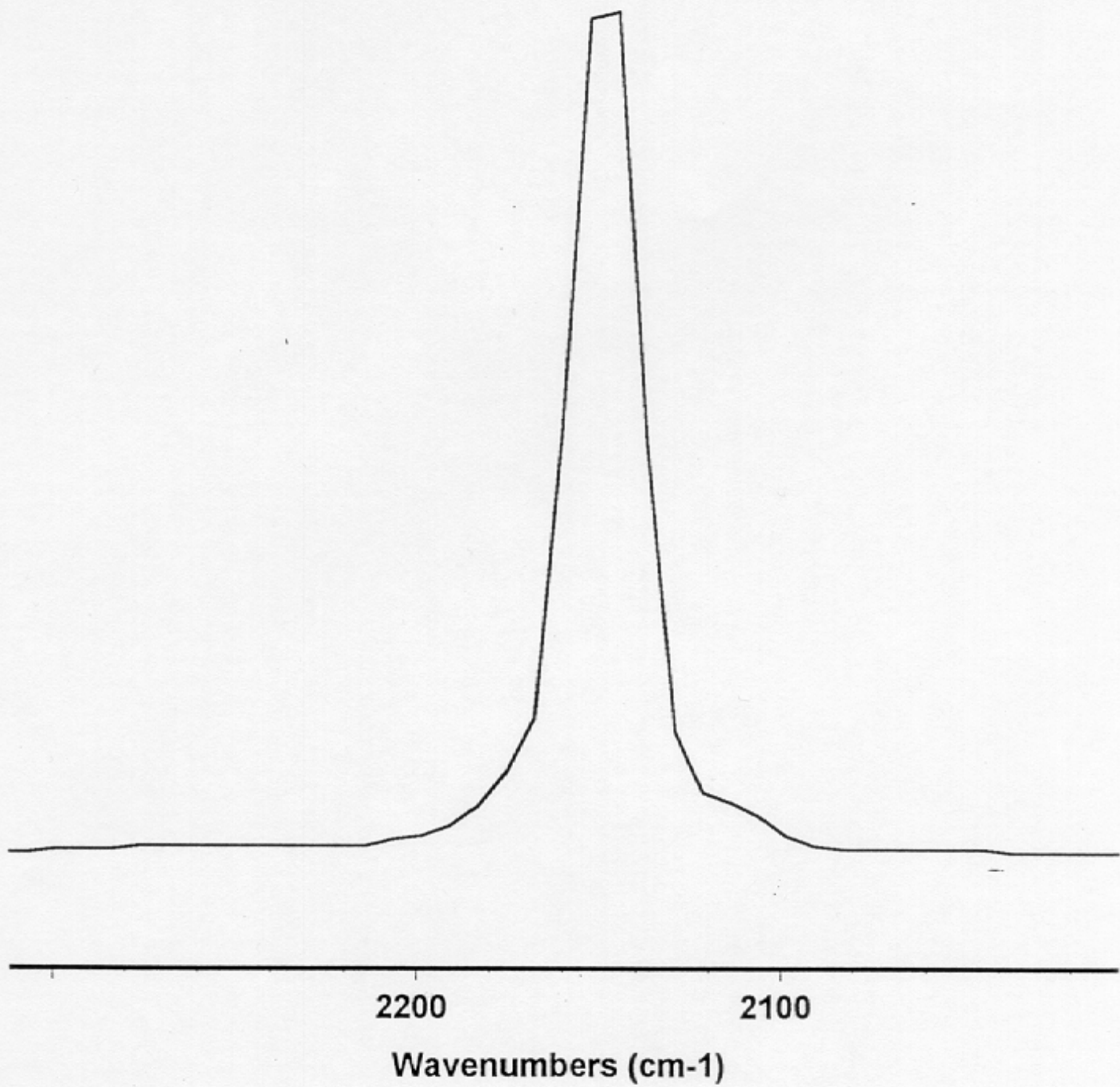


Fig. 10. An isocyanide peak (from Nicolet Spectral Libraries)

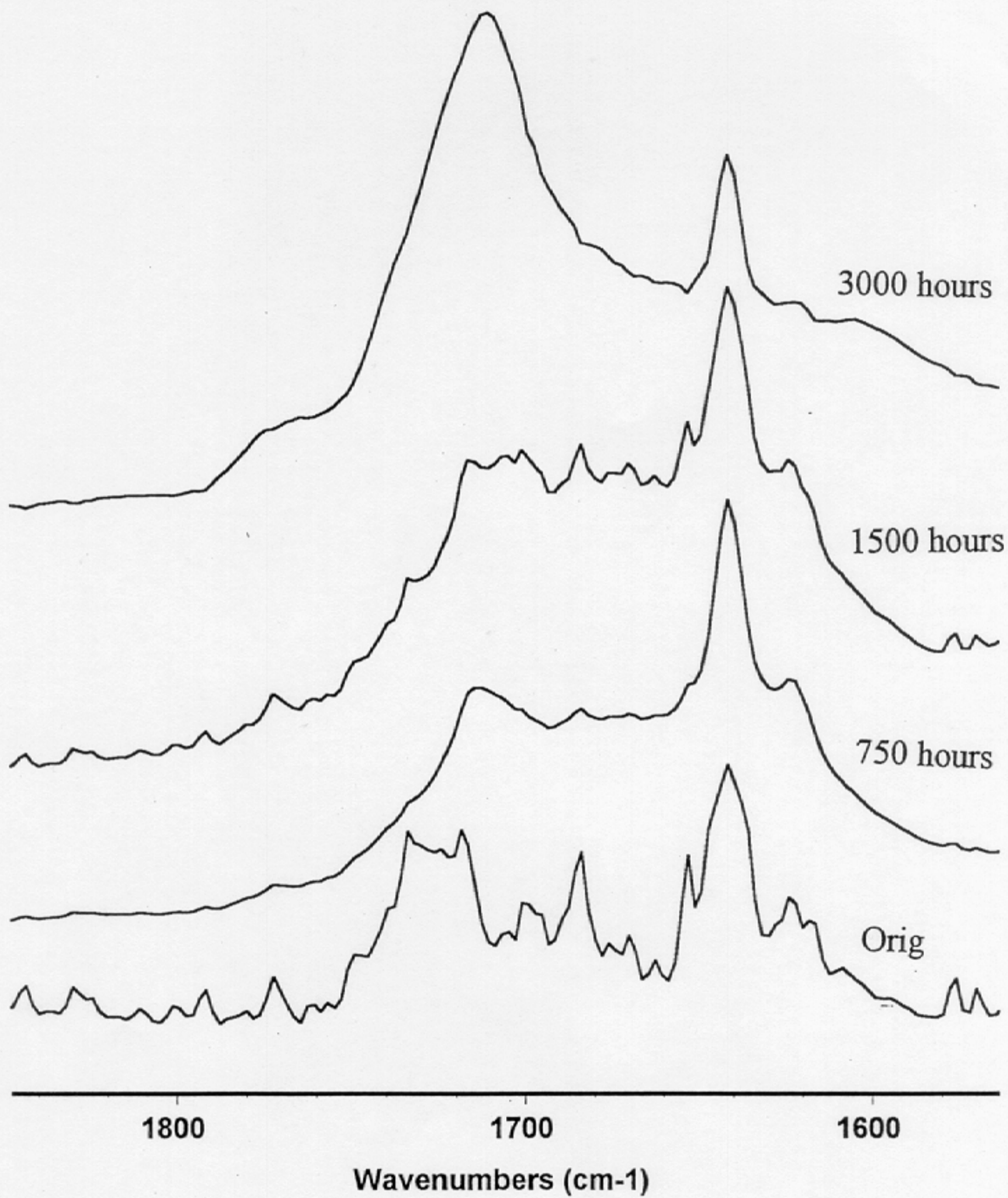


Fig. 11. Region of the FTIR spectra attributed to C=O group