

Mineral Oil and Ester Based Oil/Paper Insulation Decaying Assessment by FTIR Measurements

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Abstract. Esters based dielectric fluids have been widely researched since 1990's for application in high voltage insulation applications. Since then, researchers are affirmative towards usage of ester based insulating fluids as a replicated to mineral insulation oils. The operating properties and aging performance of ester oils proved to be potential candidates for high voltage applications. In view of high temperatures and longevity of insulation systems, there also is a need to understand the chemical perspectives along with aging behaviour of ester oils. Accelerated aging of oil/paper insulation associated with mineral oil and synthetic ester with cellulose insulant has been experimentally simulated as per ASTM D 1934 at 115°C. Fourier Transform Infrared spectroscopy analysis of oils and cellulose papers is carried out at different aging factors. The compositional changes in oils and cellulose kraft paper with aging have been enumerated. The changes in the absorbance area for appropriate functional groups have been also reported. It is found that, the chemical stability of synthetic esters is superior to that of the mineral oil.

Keywords: Transformers, Insulation, Ester oils, FTIR Spectroscopy.

1 Introduction

Since years, mineral insulating oils are been successfully used in transformer technology for insulation and cooling purposes. However, with experience, engineers realized the requirements of high dielectric and thermal performance of the insulating fluids. Consequently, mineral oil (MO) is facing some serious critiques in terms of fire point resources and biodegradability. Global research on alternative insulating fluids is affirmative towards usage of ester based dielectric fluids as a replicate to mineral ones [1]. Studies revealed that, synthetic ester (SE) is a suitable candidate for use in breather transformers and natural ester (NE) performs well in sealed transformers [2-4].

Performance of insulating oil degrade with operating times and is required to monitor periodically to ensure oil pristine conditions. Hence, there are several parameters associated with oil that are to be maintained in proper limits [5]. Dielectric and physi-

ochemical parameters of synthetic esters and natural esters have been widely investigated and is established that, ester based fluids are superior to mineral oils [ref]. Insulating oil is used in conjunction with insulation paper and hence the compatibility of new insulating oils with paper is to be ensured. Researchers have investigated the performance of insulation paper in various insulating oils and reported the reduced degradation of cellulose papers in new oils [6, 7].

The change in the quality of oil in transformer may be attributable to several reasons including electrical stress, thermal stress, and oil/paper interface properties. It is to be noticed that, these attributes involves in changing the chemical state of the oil/paper insulation. This is because, aging of oil involves in formation of aging products like acids, dissolved decay contents, dissolved gases, polar solvents and sludge which hinders the performance of insulation system. Aging of paper is also evident with production of some chemicals like furfurals, methanol, and acids. The degradation aspects of oil/paper insulation is involved with several chemical changes. Thus, there is a need to study the changes in chemical compositions that occur with aging of oil/paper insulation. Fourier Transform Infrared spectroscopy (FTIR) analysis of oil/paper insulation based on mineral oil and cellulose insulant have been reported in [8, 9]. Also, chemical compositional changes for natural ester and cellulose based insulation have been reported by researchers [10]. Comparative FTIR analysis of mineral oil, natural ester, and synthetic ester is also reported by researchers [11].

In this paper, FTIR analysis of oil/paper insulation associated with mineral oil and synthetic ester have been reported for different aging factors. FTIR analysis of mineral oil, synthetic ester, and kraft paper (aged in MO and SE) have been reported. It is noticed that, surface interaction of synthetic ester with cellulose kraft showed a significant stability in its chemical structure as compared to that of the mineral oil.

2 Experimental

Initially, mineral oil, synthetic ester, and cellulose kraft paper were subjected to drying in order to remove moisture. Dry oils and papers are transferred to aging cells and are later subjected to thermal aging as per ASTM D 1934. Oil/paper ratio adopted is 10:1, which is universally followed for oil/papers insulation studies for transformers. Thermal aging followed 500, 1000, 1500, and 2000 hours of test durations at 115°C. After every test duration, FTIR characterization is carried out for insulation oils. Simultaneously, cellulose kraft papers aged in mineral oil and synthetic ester are subjected to degreasing in hexane fumes for one hour to remove the traces of oil absorbed by cellulose fibres. Later, aged and degreased cellulose kraft papers are also subjected to FTIR characterization. In order to establish the base line prior to aging, fresh mineral oil, fresh synthetic ester and unused cellulose kraft paper are also subjected to FTIR. The peaks obtained during FTIR characterizations are compared and analysed to comment on the compositional changes with aging.

3 Results and Discussion

To understand the changes in chemical composition of oil/paper insulation with aging, different aging factors have been simulated under laboratory conditions. The changes in the surface functional groups are monitored by FTIR.

3.1 FTIR Spectrum of Mineral oil

FTIR spectra of fresh and aged MO at various aging factors is presented in Fig. 1.

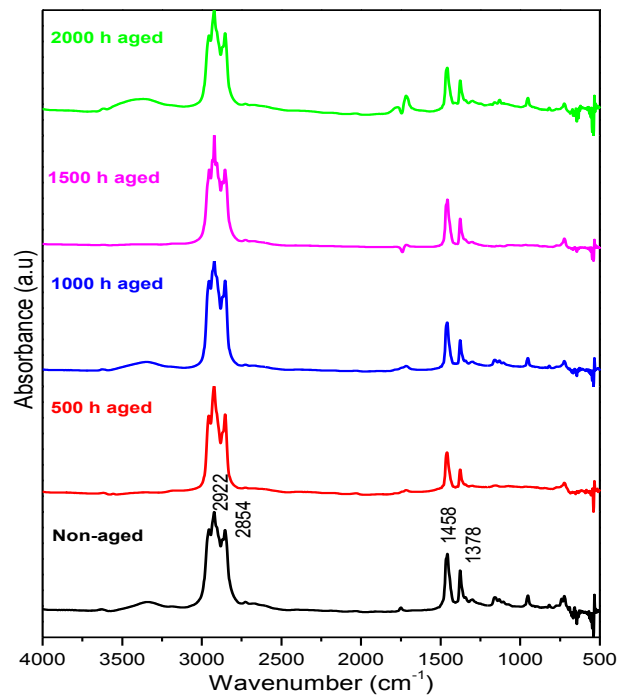


Fig. 1. FTIR spectra of fresh and aged MO

Broad O-H stretching vibration is observed in the fresh and aged samples. However, intensity profile of O-H peaks is noticed to be low. Fig. 2(a) shows the high frequency FTIR regions for peak positions of 2922 and 2854 cm^{-1} . These peaks are attributed to $-\text{CH}_2$ vibrations accompanied by a small peak at 2954 cm^{-1} that is related to $-\text{CH}_3$ vibrations [9]. The polar type of hydrocarbon bonds are the internal chemical signatures of MO. The degradation performance of MO is studied by observing the peak area under CH bonds for different aging conditions as shown in Fig. 2(b). The hydrocarbon group from the 2000 h MO showed decrease in the CH bond peak area compared to the fresh MO.

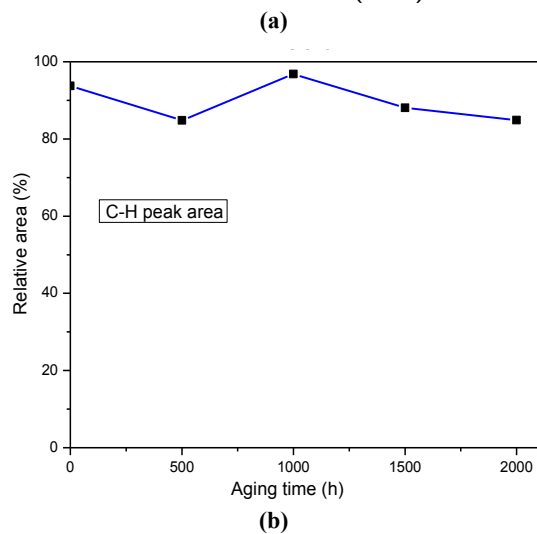
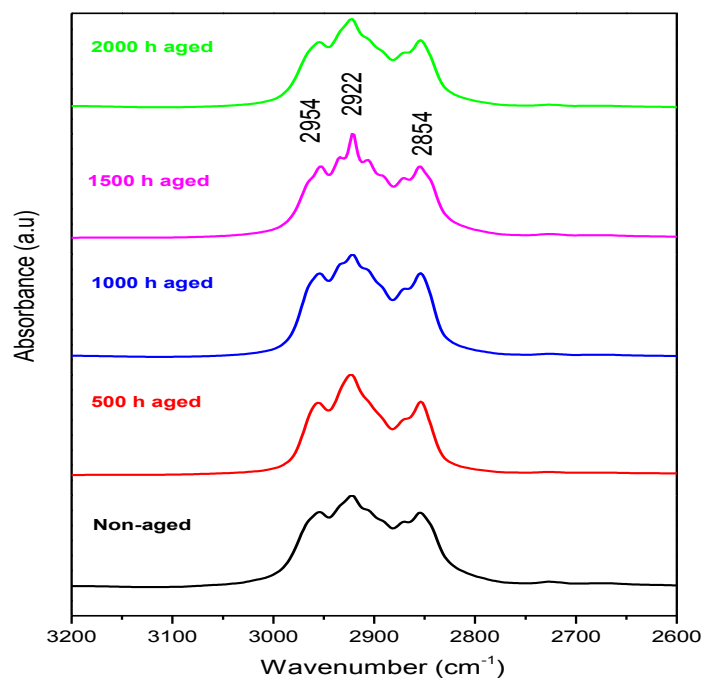


Fig 2. (a) Mineral oil peak positions at 2954, 2922 and 2854 cm^{-1} (b) the corresponding area quantifications

FTIR spectrum of peak positions for 1458 and 1378 cm^{-1} are presented in Fig. 3. The peak positions are attributed to $-\text{CH}_2$ bending vibrations that result in the similar trend as the main $-\text{CH}_2$ and $-\text{CH}_3$ vibrations.

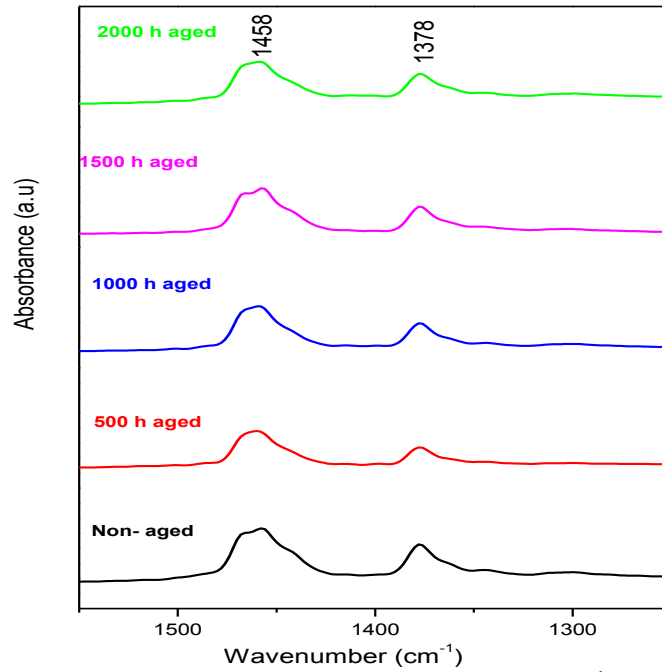


Fig. 3. Mineral oil peak positions of 1458 and 1378 cm^{-1} .

3.2 FTIR Spectrum of Synthetic Ester

FTIR spectra of fresh and aged synthetic ester at 500, 1000, 1500 and 2000 hours are presented in Fig. 4.

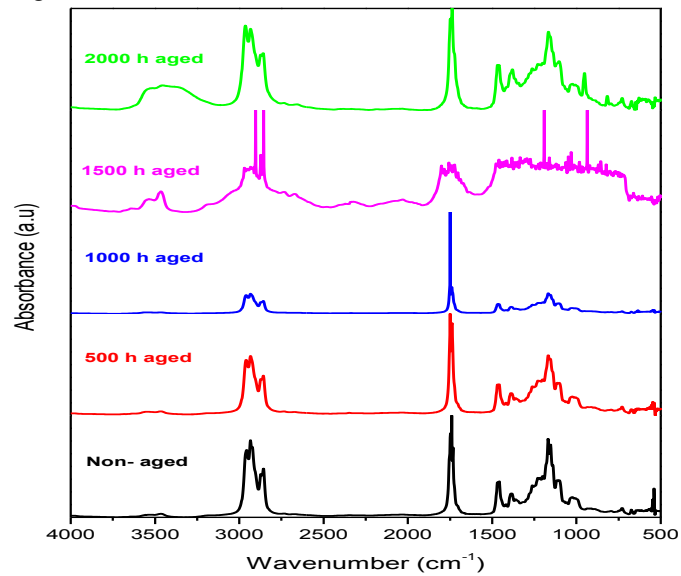


Fig. 4. FTIR spectra of SE at different aging conditions

The chemical signature of synthetic ester resulting as CH_2 and CH_3 vibrations are noticed at the peak positions of 2854 and 2922 cm^{-1} respectively. In addition, $\text{C}=\text{O}$ peaks positions are also observed in all the samples at 1750 cm^{-1} . To understand the influence of surface oxidation on synthetic ester, hydroxyl peak (OH) at $3200\text{-}3500\text{ cm}^{-1}$ is quantified and the relative area is shown in Figure 5. The relative increase in the intensity of OH vibrations at higher aging times is related to surface oxidation of its chemical structure (see Fig. 5(b)) [11]. Similarly, ester's signature peak of carboxyl group for aging factors and corresponding relative area is plotted in Fig. 6.

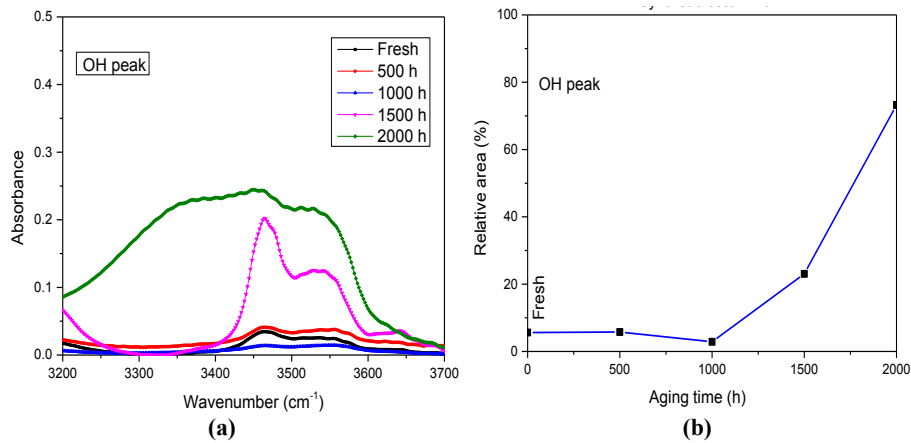


Fig. 5. (a) FTIR peak position at $3200\text{-}3500\text{ cm}^{-1}$ and its (b) corresponding peak area (SE)

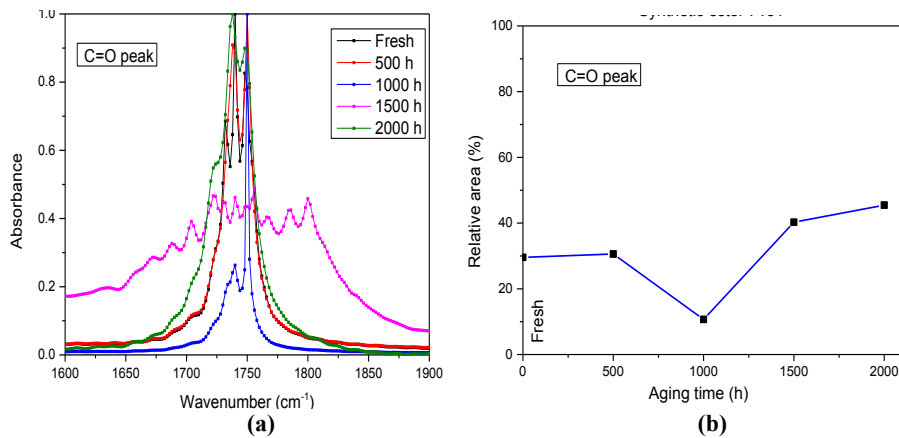


Fig. 6. (a) FTIR peak position at 1750 cm^{-1} and its (b) corresponding peak area (SE)

The relative area associated with $\text{C}=\text{O}$ peaks is observed to increase with aging of insulation. However, the percentage relative area at different aging factors at 1500 and 2000 h resulted in a small change as compared to fresh SE.

3.3 FTIR Spectrum of Cellulose Kraft Paper Aged in MO and SE

Further, to understand the properties of oil/paper interactions and their changes in the chemical structure. Aging of MO and SE is carried out in presence of cellulose. Kraft paper is degreased in hexane fumes to remove the traces of oil absorbed by cellulose fibres. Degreasing is done in order to observe the chemical compositional changes that occur in the insulation paper with aging of oil/paper insulation. The FTIR peaks of degreased kraft paper aged in mineral oil at different aging factors is presented at Fig. 7.

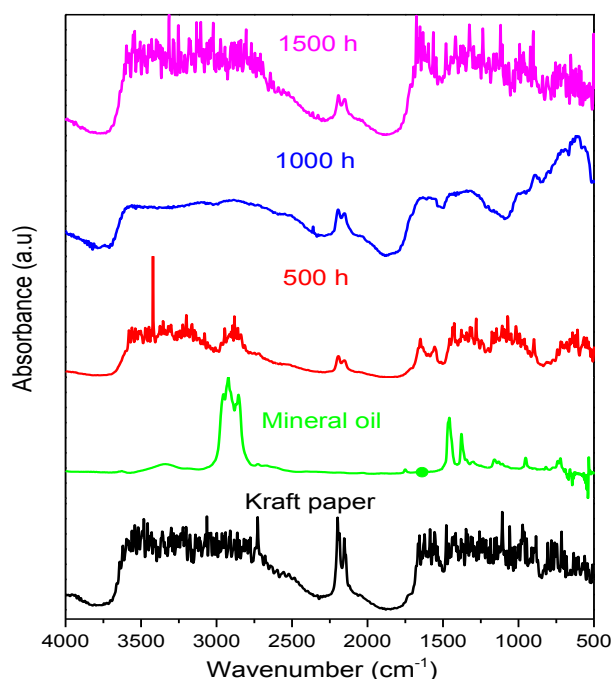


Fig. 7. FTIR spectra of cellulose Kraft paper aged in Mineral oil

Fresh and dehydrated kraft paper showed the broad range of signature at the hydroxyl group from 3500 to 3000 cm⁻¹. This is the result of atmospheric OH interaction with the chemical structure of cellulose. Apart from this, the strong absorbance peak at 2200 cm⁻¹ is a result of C≡C functional group from the cellulose structure. In fingerprint region, below 1500 cm⁻¹, very less information observed. In comparison to the fresh kraft paper, kraft paper aged in MO shows a distinct feature at around 1700 cm⁻¹. This is attributed to the C=O vibrations as a result of oil interaction with cellulose during aging [10]. To understand the decomposition of C≡C functional group, aged samples of 2200 cm⁻¹ is plotted as shown in Fig. 8.

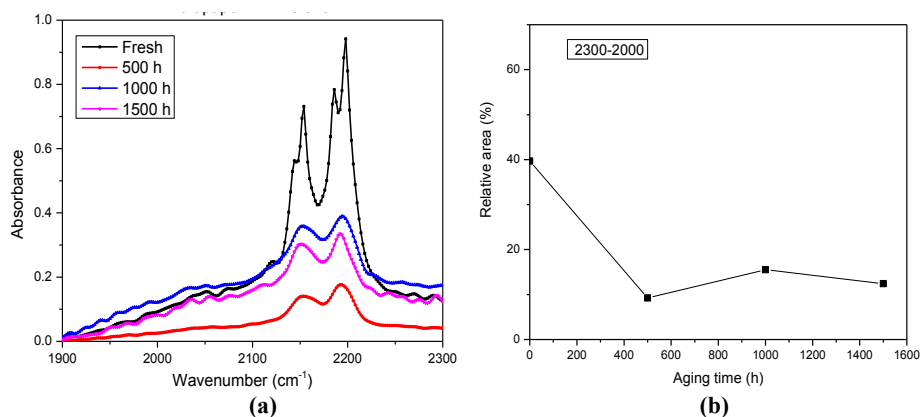


Fig. 8. (a) FTIR peak position at 2200 cm⁻¹ and (b) the corresponding relative peak area of cellulose paper aged in MO

There are two distinct signatures observed at 2150 and 2200 cm⁻¹ which is ascribed to alkynes of C≡C. The calculated relative peak area indicate a significant decrease in quantity of C≡C for aged samples. This correspond well with the appearance of new peak of C=O at 1700 cm⁻¹. FTIR spectra of degraded kraft paper aged synthetic ester in illustrated in Fig. 9.

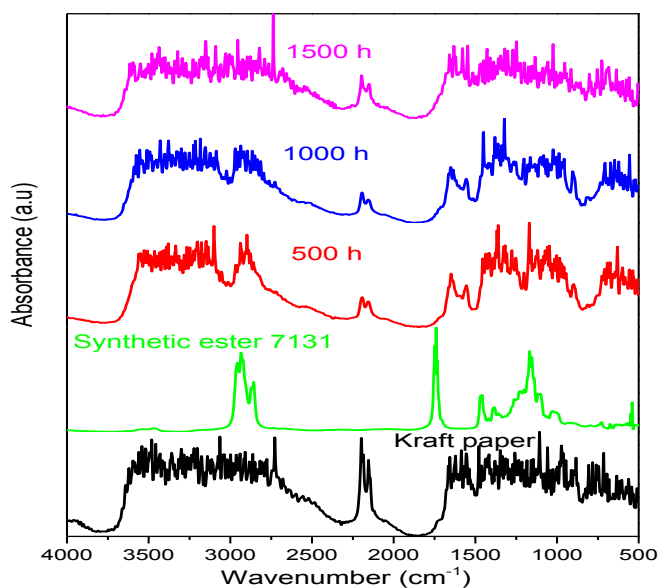


Fig. 9. FTIR spectra of cellulose Kraft paper aged in SE

Distinctive signature of cellulose C≡C functional group is observed for kraft paper aged in SE. However, the intensity of C≡C vibrations decreased due to the surface coverage of synthetic ester on the cellulose chemical structure. In addition, the signatures of -CH₂ and CH₃ vibrations are clearly observed along with the cellulose structure at 2854 and 2954 cm⁻¹. The C=O signa-

ture at 1700 cm^{-1} on ester internal chemical structure has a shift when it reacted with cellulose on aged samples. However, the shift was observed at 1650 cm^{-1} along with the new peak appeared at 1550 cm^{-1} . These peaks were attributed to C=O and C=C respectively. Similarly, the functional group of C=C vibrations are used for quantification analysis and the relative area shows much lesser degradation than the mineral oil. The corresponding peak area and quantification results are shown in Fig. 10.

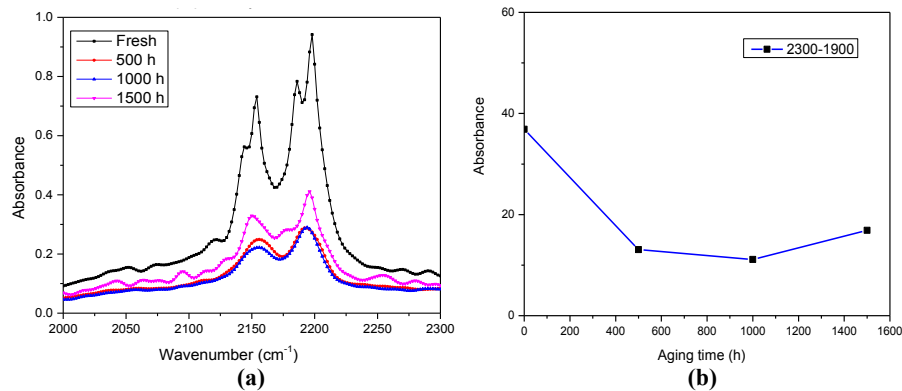


Fig. 10. (a) FTIR peak position at 2200 cm^{-1} and (b) Corresponding relative peak area of cellulose paper aged in SE

4 Conclusion

FTIR spectra of fresh and aged samples of mineral oil and synthetic ester are studied at different aging durations at 115°C . The spectrum of mineral oil showed distinctive peaks positions of its internal chemical structures at CH_2 and CH_3 vibrations. The corresponding quantification analysis confirmed very small reduction in its peak area. Similarly, synthetic ester displayed the important C=O vibrations. Chemical stability of synthetic esters under different aging times confirmed the strong surface property of synthetic ester by relative area quantification. Compared to the surface interaction of mineral oil with Kraft paper under different aging conditions, synthetic ester showed significant stability in its chemical structure. This could be due to its internal chemical structure and the presence of C=O group on its structure.

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