

Photostability of PVC Films by using Safety Synthetic Biolubricant as Additives[†]

Emad Yousif^{1*}, Rahimi M. Yusop² and Dina S. Ahmed³

¹Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq

²School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

³Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad 64021, Iraq

*Corresponding author e-mail: emad_yousif@hotmail.com

Stabilization standards of poly(vinyl chloride) (PVC) films fundamentally depend on essential laws: solvation and "reverberation" stabilization. The photo-stabilization of PVC films by epoxidized oleic acid was investigated. Photo-stabilization activities were determined by monitoring the carbonyl, polyene and hydroxyl indices with irradiation time. The changes in viscosity average molecular weight of PVC with irradiation time were also tracked using tetrahydrofuran as a solvent. The quantum yield of the chain scission (ϕ_{cs}) was evaluated and found with range $4.53E10^{-8}$ and $8.12E10^{-8}$. Postulated mechanisms were outlined depending on the structure of the additive.

Key words: UV-light; photostabilizer; poly(vinyl chloride); epoxidized oleic acid; carbonyl; polyene; hydroxyl; indices; irradiation time; viscosity; molecular weight; quantum yield; chain scission

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There is an extraordinary enthusiasm at present in the photo-degradation of polymeric frameworks, and this is reflected in the significant number of research articles that seem every year in this branch of knowledge. Temperature, humidity, and solar radiation are the main impacts that cause degradation in polymers [1]. Presentation to daylight can have unfriendly consequences for the awesome helpful enthusiasm of plastic items. Ultraviolet radiation can destroy the bonds between atoms in a polymer. Photo-degradation debasement reasons splitting, chalking, shade changes, and the loss of physical characteristics [2]. Poly(vinyl chloride) is a polymer which is extremely delicate to the weathering activity, and this limits its external applications. This happens primarily because of changes in mechanical characteristics and colour [3]. PVC is a standout amongst the broadest thermoplastic materials on the planet because of its significant characteristics, a wide range of applications, resistance, and low cost [4]. In any case, PVC suffers from poor thermal and light stability. It experiences fast autocatalytic dehydrochlorination from presentation to high temperature and light amid its moulding and utilization, individually [6, 5]. There are a few methods for avoiding UV degradation in plastics by utilizing stabilizers or blockers. Light stabilizers are utilized broadly as a part of plastics, beauty care products, and films. The principle reason for UV stabilizer is to keep polymers from photo-

degradation brought on by light displayed in daylight and other light sources [7].

As part of our on-going research in the photostabilization of poly(vinyl chloride) [8-11], the photostabilization of PVC was studied using epoxidized oleic acid as an additive.

EXPERIMENTAL

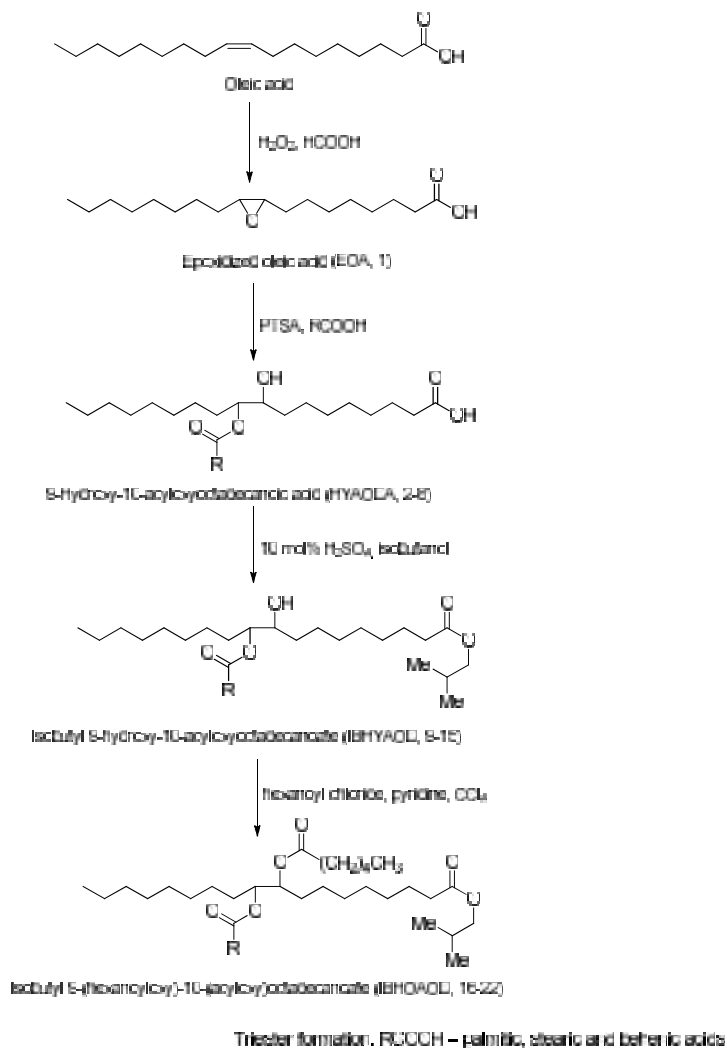
Synthesis of Epoxidized Oleic Acid

The following epoxidized oleic acid compounds in (Scheme 1) were prepared by the method has been previously described [12].

Film Preparation

Commercial PVC supplied by Petkim company (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 hours. Fixed concentrations of PVC solution (5 g/100 ml) in tetrahydrofuran were used to prepare polymer films with 40 μm thickness (measured by a micrometertype 2610 A, Germany). The prepared compounds (0.5% concentrations) were added to the films starting at 0 concentrations (blank). The films were prepared by evaporation technique at room temperature for 24 hours to remove the possible residual tetrahydrofuran solvent, film samples were

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Scheme 1. Epoxidized oleic acid compounds.

further dried at room temperature for three hours under reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

Irradiation Experiments

Accelerated testing technique. Accelerated weatherometer Q.U.V. tester (Q. panel, company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains a stainless steel plate, which has two holes in the front side and a third one behind. Each side includes a lamp (type Fluorescent Ultraviolet Lights) of 40 Watt each. These lamps are of the type UV-B 313 giving spectrum range between (290-360) nm with a maximum at wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on the samples. The irradiated samples were rotated manually from time to time to ensure that the intensity of light incident on all samples is the same.

Photodegradation Measuring Methods

1st. Measuring the photodegradation rate of polymeric films using infrared spectrophotometry. The degree of photodegradation of polymeric film samples was followed by monitoring FTIR spectra in the range (4000-400) cm^{-1} using FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified at 1722 cm^{-1} , polyene group at 1602 cm^{-1} and the hydroxyl group at 3500 cm^{-1} . The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl, polyene, and hydroxyl peaks. Then carbonyl (I_{co}), polyene (I_{po}) and hydroxyl (I_{OH}) indices were calculated by comparison of the FTIR absorption peak at 1722, 1602 and 3500 cm^{-1} with reference peak at 1328 cm^{-1} attributed to scissoring and bending of CH_2 group, respectively. This method is called the band index method [12, 13]:

$$I_s = \frac{A_s}{A_r} \quad (1)$$

The functional group index (I_s) is dependent on both the absorbance of the peak under study (A_s) and that for the reference peak (A_r).

2nd. *Determination of average molecular weight using viscometry method.* The viscosity property was used to determine the average molecular weight of polymer at room temperature, using the Mark- Houwink relation [14]:

$$[\eta] = K\bar{M}_v^a \quad (2)$$

where, $[\eta]$ = intrinsic viscosity; K , a are constants depend upon the polymer-solvent system at a particular temperature.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (g/100 ml) and the flow times of polymer solution and pure solvent are t and t_0 respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{rel} = \frac{t}{t_0} \quad (3)$$

η_{rel} = relative viscosity.

$$\eta_{sp} = \eta_{rel} - 1 \quad (4)$$

The single-point measurements were converted to intrinsic viscosities by the relation 2.

$$[\eta] = \left(\frac{\sqrt{2}}{C}\right) (\eta_{sp} - \ln \eta_{rel})^{1/2} \quad (5)$$

where, C = concentration of polymer solution (g /100 ml).

By applying Equation 5, the molecular weight of degraded and the virgin polymer can be calculated. Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution using the following equation:

$$[\eta] = 1.38 \times 10^{-4} \bar{M}_v^{0.77} \quad (6)$$

The quantum yield of main chain scission (Q_{cs}) [15] was calculated from viscosity measurement using the following relation 7.

$$Q_{cs} = (CA/\bar{M}_{v,0}) \{([\eta]_0/[\eta])^{1/r} - 1\} / I_0 t \quad (7)$$

Where, C = concentration; A = Avogadro's number; $\bar{M}_{v,0}$ = initial viscosity-average molecular weight; $[\eta]_0$ = Intrinsic viscosity of PVC before irradiation; $[\eta]$ = Intrinsic viscosity of polymer after irradiation; r = Exponent in the relation: $[\eta] = KM^r$; I_0 = incident intensity and t = irradiation time in second.

RESULTS AND DISCUSSION

The epoxidized oleic acids were used as additives for the photostabilization of PVC films. To study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl, polyene, and hydroxyl indices were monitored with irradiation time using IR spectrophotometry. The irradiation of PVC films with UV light of wavelength, $\lambda = 313$ nm led to a clear change in the FTIR spectrum. Appearance of bands in 1772 cm^{-1} and 1724 cm^{-1} , were attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone, respectively. A third band was observed at 1604 cm^{-1} , related to polyene group. The hydroxyl band appeared at 3500 cm^{-1} was annotated to the hydroxyl group [13]. The absorption of the carbonyl, polyene and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{co}), polyene index (I_{PO}) and hydroxyl index (I_{OH}). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure 1, the I_{co} of A3, A2, and A1 showed lower growth rate with irradiation time concerning the PVC blank film without additives. Since the growth of the carbonyl index with irradiation time is lower than PVC blank, as seen in Figure 2, it is suitable to conclude that these additives might be considered as photostabilizers of PVC polymer. Efficient photostabilizer shows a more extended induction period. Therefore, the A1 is the most active photostabilizer, followed by A2, and A3 which is the least active. Just like carbonyl, polyene compounds were also produced during photodegradation of PVC. Therefore, the polyene index (I_{PO}) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure 3. Hydroxyl species were produced during photodegradation of PVC. Therefore, the hydroxyl index (I_{OH}) was monitored with irradiation time for PVC and with additives. From Figure 4, the A3, A2, and A1 showed a lower growth rate of hydroxyl index with irradiation time compare to PVC film without modification (Figure 4).

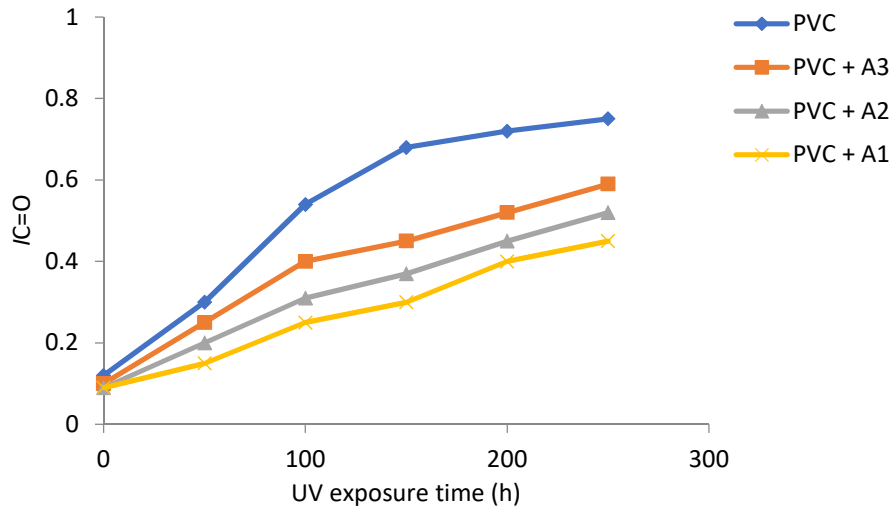


Figure 2. The relationship between the carbonyl index and irradiation time for PVC films (4 μm thickness) containing different additives.

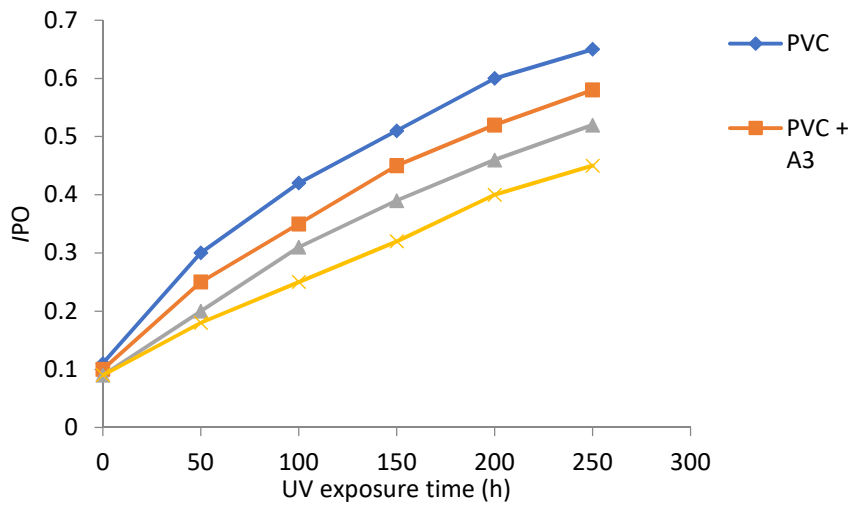


Figure 3. The relationship between the polyene index and irradiation time for PVC films (40 μm thickness) containing different additives.

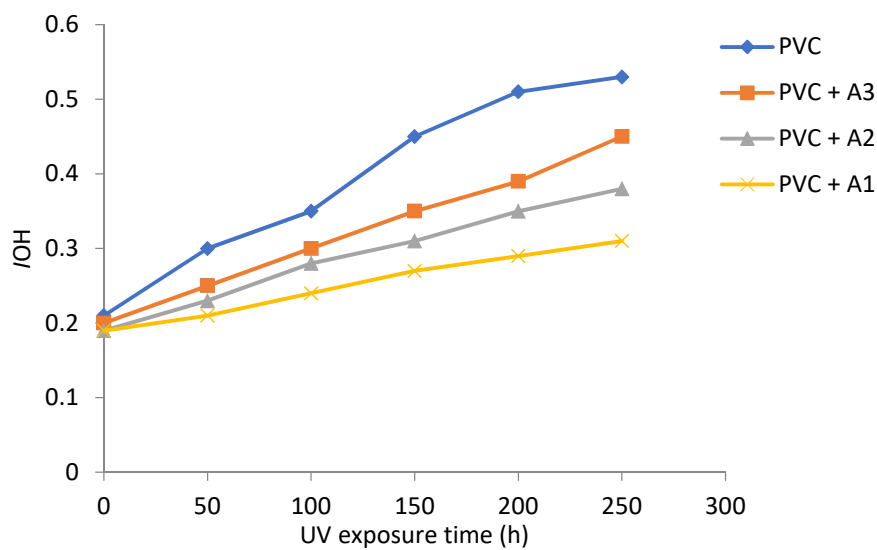


Figure 4. The relationship between the hydroxyl index and irradiation time for PVC films (40 μm thickness) containing different additives.

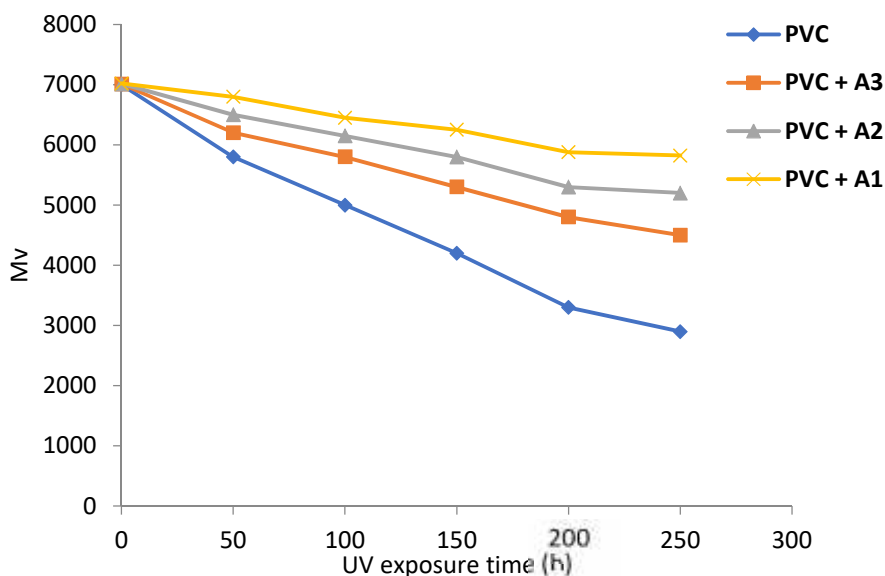


Figure 5. Changes in the viscosity-average molecular weight \bar{M}_v during irradiation of PVC films (40 μm) (blank) and with 0.5 wt% of additives.

Variation of PVC molecular weight during photolysis in the presence of epoxidized oleic acid as an additive, analysis of the relative changes in viscosity average molecular weight \bar{M}_v has been shown to provide a versatile test for random chain scission. Figure 5 shows the plot of \bar{M}_v versus irradiation time for PVC film with and without 0.5% (w/w) of the selected additives, with absorbed light intensity of $1.052 \times 10^{-8} \text{ ein.dm}^{-3}.\text{s}^{-1}$. \bar{M}_v measured by using Equation 4 with THF as a solvent at 25°C.

The degradation reaction characterization used to measure of the quantum yield of the chain scission (ϕ_{cs}). The quantum yield for chain scission was calculated for PVC films with and without 0.5% (wt/wt) of additive mentioned above using relation 7. The ϕ_{cs} values for compounds are shown in Table 1.

The ϕ_{cs} values for PVC films in the presence

of additive are less than that of additive free PVC (blank), which increase in the order:

$$\text{A1, A2, A3 and PVC} \rightarrow$$

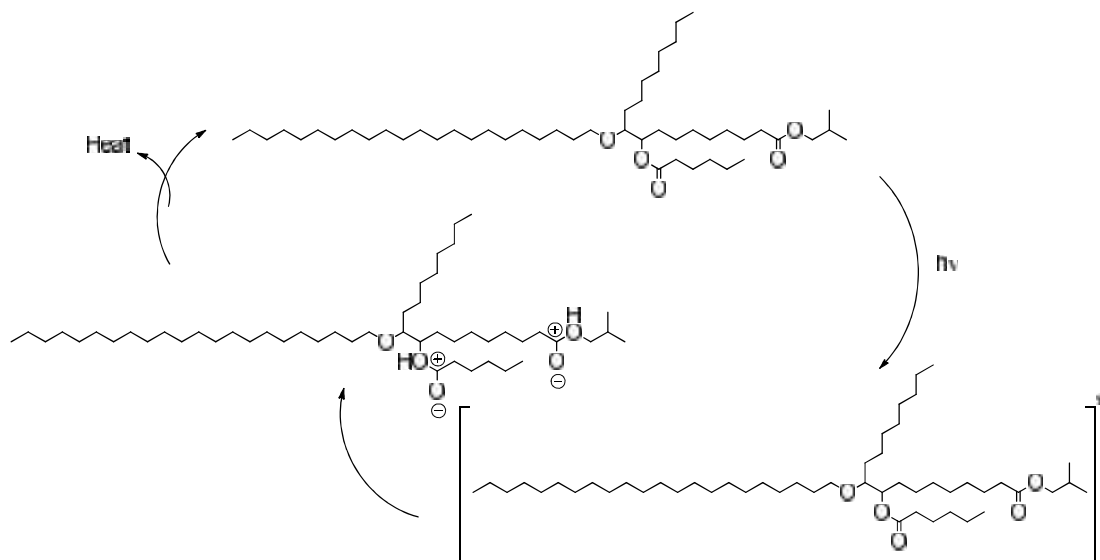
It is well established that the quantum yield (ϕ_{cs}) increases with increasing temperature [16] around the glass transition temperature.

Proposed Mechanisms of PVC Film Photostabilization

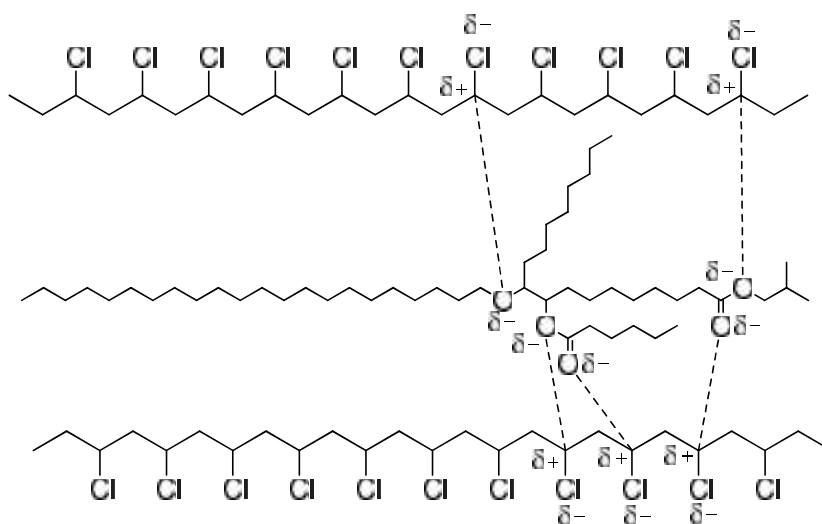
Epoxidized oleic acid compounds A1-A3 are electron rich (six aryl rings) and can absorb the UV radiation energy directly and dissipate it into harmless heat energy (Scheme 2). Aromatic compounds commonly act as UV absorbers [7, 17, 18].

Table 1. Quantum yield (ϕ_{cs}) for the chain scission for PVC films (40 μm) thickness with and without 0.5 (wt/wt) additive after 250 h irradiation time.

Sample	Quantum yield of main chain scission
PVC + A1	4.53E-08
PVC + A2	7.23E-08
PVC + A3	8.12E-08
PVC (blank)	8.33E-05



Scheme 2. PVC photostabilization of PVC *via* direct absorption of UV radiation.



Scheme 3. PVC photostabilization *via* interaction between PVC films and epoxidized oleic acid compound.

The possible attraction between polarized C=O bonds within epoxidized oleic acid compounds A1-A3 and polarized C-Cl bonds within PVC chains could stabilize PVC (Scheme 3). Such attraction could allow efficient transfer of the PVC excited energy to Schiff bases and then to a harmless level of energy [19, 20].

CONCLUSION

In the work described in this paper, the photostabilization of PVC films using epoxidized oleic acid as additive were studied. These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their

decrease in carbonyl, polyene and hydroxyl indices for PVC films.

$$A1 > A2 > A3.$$

The epoxidized oleic acid as additive was found to be the more efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using tin compounds as stabilizer for PVC.

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