

New insight into the benefits of synthetic esters in challenging lubricating applications

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Introduction

Synthetic esters have been used for over 60 years now in various lubricating applications. Their use is well known, for instance, in aviation turbine oils, air compressor oils, high temperature chain oils, 2-stroke and racing engine oils, or even ultra-low temperature hydraulic oils. However, such uses of esters have been limited to specific areas where cleanliness, resistance to high temperatures, good lubricity and added solvency are required.

Rapid, recent legislation changes on exhaust gas emissions, and subsequent new technologies and equipment, the quest for higher power density, improved energy efficiency, extended durability, as well as the growing concern over environmental impacts of lubrication are clearly paving the way towards higher performance and better sustainability for lubricants.

1 Traditional uses of synthetic esters

The use of synthetic esters is well known in a number of specific applications where their high thermal stability, superior cleanliness, natural lubricity, and polarity have long been exploited.

1.1 Polar agents

One of the most traditional uses of esters is probably as a polar additive in non-polar hydrocarbons, such as Poly Alpha Olefins. In such base fluids, diesters in particular have been used as:

- seal swell agents to mitigate seal shrinkage normally observed in such formulations;
- dispersing agents in fluids that generate sludge;
- additive solubility auxiliaries in viscous non-polar media.

1.2 Aviation gas turbines

In aircraft or ground gas turbines, neopolyol esters have been used almost exclusively for decades, for their ability to sustain temperatures of up to 220°C in bulk, with excellent deposit control on hot metal parts (up to 375°C), either in liquid or in vapour phase. In addition, excellent low temperature behaviour is also required (pour point is typically lower than -54°C), which neopolyol esters also deliver.

1.3 Air compressors

In a number of volumetric air compressors, compression chambers are lubricated (piston, vane and screw compressors), thus submitting the oil to elevated temperatures of up to 230°C typically. Esters, particularly diesters (phthalates), have been used for their low volatility, delivering cleaner air, and their low coking propensity, thus protecting the equipment against possible auto-ignition of carbonaceous deposits or valve-sticking issues leading to possible explosions.

1.4 High temperature chains

The low volatility features of esters, along with their high resistance to thermo-oxidation and low deposit formation properties, have long been taken advantage of in high temperature chain oils to minimize formation of gummy and carbonaceous residues and preserve lubricity over time. In addition, high flash points delivered by synthetic esters (up to 325°C) bring additional safety features to such products. Diesters and triesters (trimellitates) in particular have been used in such formulations.

1.5 Two-stroke engine oils

In such applications, the cleanliness of the oil in operation, its ability to decrease smoke formation, and its lubricity are key features. Diesters, thanks to their clean burning properties, natural detergency, and good lubricity, are excellent base fluid for 2-stroke engine oils. Since a portion of the fuel/oil/air mix is released unburnt to the environment (total loss lubrication), the good environmental profile of synthetic esters is also of great value.

Compared to mineral oils, synthetic esters will typically reduce wear, deposit and varnish formation, and exhaust smoke. Moreover, a reduction of up to 25% Polycyclic Aromatic Hydrocarbons content in exhaust gases has been reported [1].

1.6 Refrigeration compressors

This is a major outlet for neopolyol esters. The switch to non-ozone depleting refrigerant fluids (HFC) has generated the need for highly polar lubricants, showing good miscibility and chemical compatibility features with HFC. Neopolyol esters also show good cold flow properties, high thermal stability, and excellent lubricity.

2 Structure/performance relationships

2.1 Polarity

The ester chemical function displays a permanent dipole, due to oxygen electronegativity (Figure 1). This intrinsic polarity has a number of consequences and imparts specific properties of interest from a lubrication standpoint:

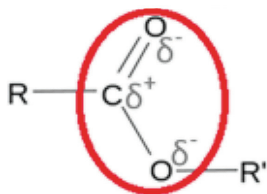


Figure 1. Permanent dipoles in esters

- Permanent dipoles attract each other through electrostatic forces. Such intermolecular forces are roughly 100 times weaker than covalent bonds and 5 times weaker than hydrogen bonds [2]. They impart greater internal cohesion than in pure hydrocarbons, resulting in lower volatility and evaporation rates (4 mm²/s @ 100°C neopolyol ester is able to show a NOACK volatility – 1h @ 250°C of roughly 7%), and consequently higher flash points. Synthetic esters may show flash points of up to 310°C at ISO VG 46 (Figure 2). Additionally, long, linear carbon chains in ester structures further reduce volatility.

Property	Unit	Naphthenic	Gr I	Gr II	PAO	Alkyl Naphthalene	Diester	Neopolyol ester	Complex ester
Viscosity at 100°C	mm ² /s	4.6	5.0	5.1	5.1	4.8	5.3	4.9	5.7
Viscosity at 40°C	mm ² /s	31.3	29.8	26	24.1	28.7	26.6	22.6	28
Flash point COC	°C	194	195	226	245	232	234	267	265
Evaporation by TGA 250°C – 1 h*	%	43.4	38.3	19.3	5.6	12.0	4.7	2.3	2.6

Figure 2. Volatility of synthetic esters vs other base stocks

- Negatively charged oxygen from ester chemical function will bind to positively charged sites of metal surfaces. In a mixed or boundary lubrication regime, esters will stick to the surface and provide protection against friction and wear, to some extent, thanks to their natural affinity with metal surfaces. As a result esters may be viewed as friction modifiers (or “lubricity agents”) capable of reducing friction coefficients and wear in moderately loaded conditions (Figure 3). Long, linear carbon chains improve anti-wear capability and friction modification.

Property	Unit	Gr I	Gr II	Alkyl Naphthalene	PAO	Diester	Neopolyol ester
Viscosity at 100°C	mm ² /s	4.18	4.25	4.82	3.95	3.56	4.40
Viscosity at 40°C	mm ² /s	21.3	19.7	28.7	17.3	13.7	19.7
4 ball Wear Scar 40 kg, 1 h	mm	1.10	0.76	0.91	0.73	0.85	0.64
60 kg, 30 min	mm	-	-	-	1.78	-	0.71
HFRR 5N – 60°C – 75 mn	mm	0.492	0.311	0.296	0.225	0.230	0.220
Friction coefficient	-	-	-	-	-	-	-

Figure 3. Friction modification of synthetic esters vs other base stocks

- The co-existence of polar sites with non-polar hydrocarbon chains gives esters amphiphilic properties: they show dispersancy and detergency features. As a result, esters do contribute to minimizing the formation of deposits and varnishes on surfaces and help keep oxidation products in suspension. In addition, esters will also help dissolve poorly soluble additives in non-polar base fluids, through similar mechanisms.

- Esters (diesters in particular), are very good plasticizers. Their polarity makes them interact with a number of polymers. The measurement of the Anilin Point (ASTM D611), initially used as an indicator of the aromaticity of oils, may also supply an estimate of the potential effect of esters on polymers. Esters typically show Anilin Points revolving around 10°C, which is much lower than any hydrocarbon, including naphthenics or aromatics. As a consequence, esters may be used as seal swelling agents, especially in non-polar media, where elastomeric seals may shrink (Figure 4). Using long, linear chains in esters mitigate the impact on elastomers and improve seal compatibility if needed.



Figure 4. Anilin point of various base stocks

2.2 Thermo-oxidative stability of esters

2.2.1 Thermal stability

At elevated temperatures, esters undergo thermal degradation phenomena, in which oxygen do not play any role. From that standpoint, the ester chemical function may be viewed as a weak point, as it may undergo β -elimination, leading to alkenes and acids (Figure 5). Such a reaction is probably becoming significant at temperatures of 275°C to 315°C. However, metals like iron or copper will have a strong catalytic effect and will dramatically lower the temperatures at which this reaction takes place to about 200°C [3].

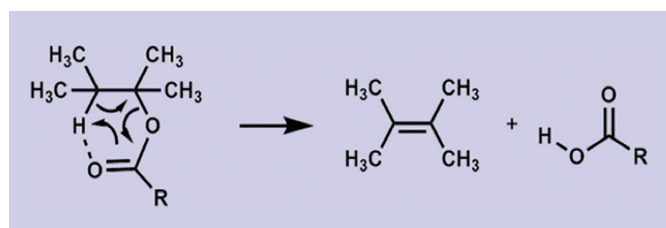


Figure 5. β -elimination

Using neopentyl structures (Figure 6), in which no hydrogen is present in β position of oxygen, suppresses any possibility of β -elimination and greatly improves, *de facto*, the thermal stability of esters. Such structures are called neopolyol esters.

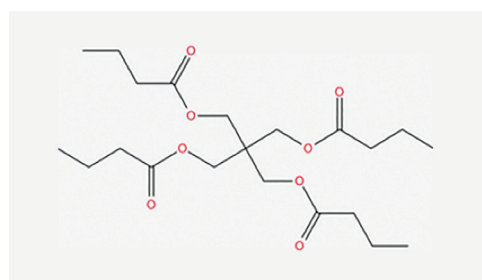


Figure 6. Neopentyl structure

2.2.2 Resistance to oxidation

The first step of the commonly accepted oxidation mechanisms is the abduction by oxygen of a hydrogen atom, thus producing a free radical. $-\text{CH}_2-$ groups from alcohol chains are expected to be highly reactive, however they are protected by steric hindrance from acid chains on neopolyol esters. As a result, $-\text{CH}_2-$ groups from acid chains are the main sites of oxygen attack [4].

On the acid chain, hydrogen atoms exhibit different reactivities towards oxygen, depending on their positions. Hydrogen atoms bonded to tertiary and secondary carbons are the most likely to be oxidized, i.e. $-\text{CH}-$ and CH_2- groups. This is directly related to the thermodynamic stability of the resulting free radical. Therefore, if the number of $-\text{CH}_3-$ hydrogens increases with respect to the number of $-\text{CH}_2-$ and $-\text{CH}-$ hydrogens, the kinetics of the oxidation reactions will slow and oxidation stability will increase [3]. The direct consequence of this is:

- the shorter the acid chains, the more stable the structure against oxidation (less $-\text{CH}_2-$);
- the more branched the acid chains, the more stable the structure against oxidation (more $-\text{CH}_3-$, added protection from steric hindrance) (Figure 7).





ASTM D4636 204°C	Test tube	Deposits
C8-C10 ester		
Iso-C8, iso-C9 ester		

Figure 7. Oxidation and corrosion test ASTM D4636

Oxidation reactions, like thermal degradation reactions, are strongly catalyzed by transition metals (iron in particular).

2.2.3 Coking propensity

Whatever their structure, esters (like any other compound) will eventually start to degrade at elevated temperatures. For ultra-high temperature applications (oven chains oils for instance), the question of what happens when the oil practically "burns" must be raised:

- it may polymerize, get viscous, and generate sludge and insoluble particulate matter;
- it may generate coke (hard, carbonaceous deposits on surfaces);
- it may also decompose and break down into light, volatile fractions, in a kind of pyrolytic mechanism.

Esters were reported to show gas evolution during oxidation process (CO_2 , H_2 , and CO) [5], and some structures will favour such decomposition pathways that preserve cleanliness in

operation over polymerization and coking mechanisms. It is believed that highly branched structures in particular will favour such chemical decomposition reactions (Figure 8).



Figure 8. Micro-Coking Test, 230-280°C
GFC-Lu-27-A-13

Cleanliness is not only a matter of resistance to oxidation: it is also linked to the ability of an oil to decompose cleanly. Highly branched neopolyol esters will strongly resist elevated temperatures and will eventually decompose cleanly, leaving little or no residue. A fully branched neopolyol ester, for instance, will start showing initial signs of degradation at roughly 210°C.

2.2.4 Additives

Anti-oxidant response is excellent in esters in general. Preferred antioxidants are generally alkylated diphenylamines. Also, taking in consideration that metals (iron and copper in particular) do catalyze oxidation reactions, any additive capable of deactivating such a catalytic effect will have a positive impact on oxidation resistance. Phosphorus additives are useful for inhibiting catalytic effect of iron, whilst metal deactivators like heterocyclic compounds are used to passivate yellow metals. Additives play a major role in the high temperature performance of synthetic esters.

2.3 Biodegradability

The ester chemical function can be degraded by bacteria. It is believed that the initial step of this process is hydrolysis of ester. As a consequence, esters that are highly hydrolytically stable tend to show low biodegradability features, even though this is not verified for all esters.

The majority of esters do show high levels of biodegradability as measured according to OECD 301B (typically 70-80%, up to 100%). They generally show higher biodegradability levels than any other base stock. In addition, whilst oil soluble PAGs or PAOs for instance only demonstrate significant biodegradability for the lower viscosity grades, synthetic ester technology is not limited by viscosity: 79% biodegradability (OECD 301B) can be achieved with an ISO VG 1000 synthetic ester.

2.4 Esters are designed

Synthetic esters are produced from defined, mostly pure raw materials. These alcohols and acids may be chosen from a variety of available compounds. This ultimately means that:

- Synthetic esters are mostly pure materials. The chemical structures are usually well defined and they are composed of a very limited number of compounds, if not one single molecule. There is not any undesirable material in the base fluid, and properties and the behaviour of synthetic esters remain very consistent in operation, thus ensuring optimum performance.
- Mineral or organic impurities may have a significant impact on the performance of the base fluid. Synthetic esters are clean products, which means they do not contain impurities or other compounds not introduced deliberately that may be detrimental to quality – provided the manufacturing process is optimized that way.
- The chemical structure of synthetic esters can be chosen. Trade-offs do exist with synthetic esters, and one may choose to maximize some properties over others, and minimize undesirable features. This can be achieved through careful design of the structure to match, as closely as possible, lubricating needs. This gives some precious flexibility to formulators.
- Whilst most neopolyols derive from petroleum industry (even though biosourced alcohols are coming up), fatty acids may be chosen from vegetable sources, thus allowing the production of esters showing high contents of renewable carbon. This content may be as high as 100% but typically revolves around 70 to 80%.

Synthetic esters constitute a large family of compounds, which may be very different in performance from one another. However, most of them will offer a unique combination of high performance features, including low volatility, high viscosity indices, low pour points, excellent thermo-oxidative stability and low propensity to deposit formation, excellent lubricity, whilst showing a very good environmental profile.

3 Esters in modern, challenging lubricating applications

3.1 Tougher requirements in modern lubrication

Market drivers are clearly changing the world of lubrication by promoting:

- higher power density,
- higher energy efficiency,
- increased durability,
- lower environmental impact,
- more sustainability,
- improved safety.

This translates into new legislation prompting OEMs to issue specifications that reflect this in simple terms: added power density, energy efficiency, and durability, whilst environmental impact should be minimized.

From the lubricant manufacturer's point of view this translates into:

- stronger oxidative stress on lubricants,
- reducing friction, possibly by reducing viscosity,
- keeping volatility at a low level,
- harmless, biodegradable and renewable lubricants.

The following is a number of examples of how synthetic esters may contribute to developing such modern – or future – lubricants.

3.2 Latest generation Passenger Car Motor Oil

The future 4-stroke engine oils will have to be:

- thinner, for fuel economy improvement;
- submitted to higher temperatures, for longer times, for better energy efficiency and durability;
- submitted to the increasing presence of biofuels.

Therefore 4-stroke engine oils will have to show lower volatilities, higher thermo-oxidative stabilities, and improved cleanliness features. This is typically what high performance esters should be able to deliver.

A laboratory experiment was conducted, in which 5W-30 oils, one being ILSAC GF-5 compliant, and the other ACEA C1-2012 compliant, were modified by replacing 20% of PAO 4 by a neopolyol ester of equivalent viscosity. Looking at the neopolyol ester properties (Figure 9), improved cleanliness, weaker deposit formation, and lower volatility are expected with this change.

	PAO 4	POLYOL ESTER
KV40	3.9	4
KV100	17.4	17.4
VI	124	134
Pour Point	-68	-63
CCS-35	1424	1766
NOACK	13.2	6.4

Figure 9. Comparison between 4 mm²/s synthetic fluids

The Micro-Coking Test clearly demonstrates improved deposit formation features with the oils that contain the ester (Figure 10).





MCT 230-280	GF-5	GF-5 + ester	C1-2012	C1-2012 ester
TDD	232,00	243,00	248,00	248,00
Merit A	7,68	8,59	5,26	7,68
Merit B	8,39	9,02	9,64	9,75
Moyenne	8,04	8,81	7,45	8,72
				

Figure 10. Micro-Coking Test, 230-280°C, GFC-Lu-27-A-13

This was confirmed on the GF-5 oils by running a TEOST 33C test that shows a 30% reduction on the total mass of deposit (Figure 11).

TEOST 33C		GF-5	GF-5 + ester
Rod Deposit	mg	18,4	13,1
Filter Deposit	mg	5	3,2
Total Deposit	mg	23,4	16,3

Figure 11. TEOST 33C (ASTM D6335)

With regards to volatility, isothermal thermogravimetric analyses display obvious reduction of the overall volatility of the modified oils (Figure 13), which is confirmed by NOACK test measurements that exhibit up to 1.6% mass loss reduction (Figure 12).

NOACK volatility (correlation by TGA – ASTM D6375)			
Oil 1 PAO4	ILSAC GF-5	9.3 %	
Oil 1 Neopolyol ester	ILSAC GF-5	7.7 %	
Oil 2 PAO4	ACEA C1-2012	12.4 %	
Oil 2 Neopolyol ester	ACEA C1-2012	11.1 %	

Figure 12. NOACK test ASTM D6375

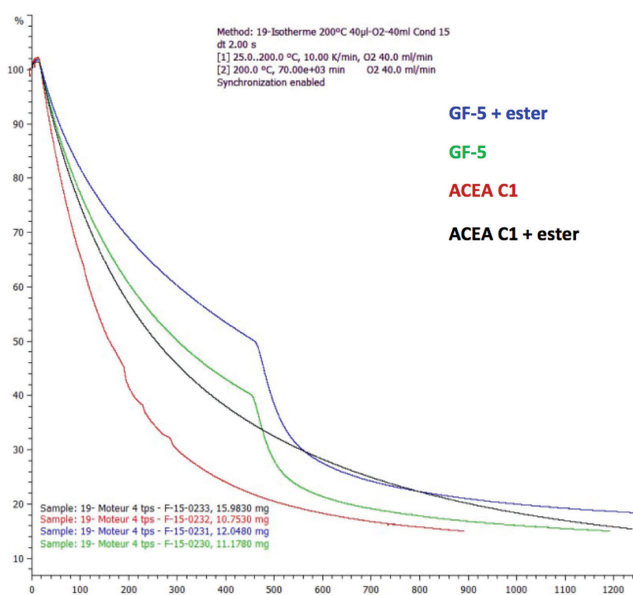


Figure 13. TGA, 200°C, O₂

3.3 Taking high temperature chain oils a step further

Specifically designed neopolyol esters (with a high amount of branched acids) do show an ideal profile in use in high temperature chain oils:

- they exhibit low volatility and resist high temperatures for a long time;
- when they start degrading, they actually decompose quickly into light, volatile fractions;
- they leave very little or no residue.

Such a behavior is significantly different from synthetic hydrocarbons, or even diesters or triesters like trimellitate, that tend to evaporate/get oxidized very quickly and leave a high amount of residue (Figure 14 and 15).

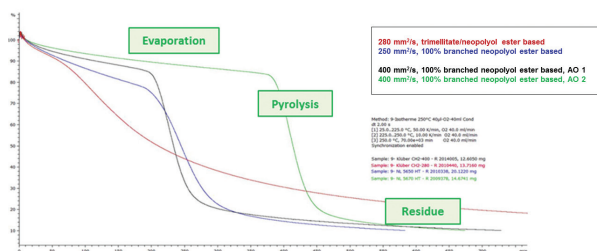


Figure 14. TGA, 250°C, O₂







Micro-Coking Test		250 mm2/s - trimellitate/iso-paraffin	250 mm2/s - branched neopolyol
230-280°C			
Deposit Temperature	°C	253	> 280
Average Merit	—	9,33	10,00
			
250-300°C			
Deposit Temperature	°C	250	259
Average Merit	—	7,86	8,58
			
280-330°C			
Deposit Temperature	°C	< 280	< 280
Average Merit	—	2,28	6,65
			

Figure 15. Micro-Coking Test on high temperature chain oils

Optimized ester chemistry, suitably additized with high performance anti-oxidants specifically developed to optimize resistance to oxidation and clean degradation, achieves outstanding high temperature performance. Temperatures of up to 300°C may be sustained on high temperature oils using such technology.

With regards to safety, such products are able to show Flash Points of more than 300°C easily.

3.4 Pushing temperature limits on greases

A high temperature chain oil as described above was thickened with both clay and silica, in order to explore the possibility of producing a high temperature grease based on neopolyol ester technology.

Whilst clay yielded a mechanically stable grease, silica, as expected, did not. However, silica proved to be more neutral towards oxidation mechanisms, whilst organically modified clay did interfere with oxidation stability.

It was however possible to obtain a grease resisting temperatures of up to 230°C, maybe more (Figure 16 and 17). Such technologies may be able to compete with some silicone based greases in a temperature area where PAO based products start being strongly unstable.

PROPERTIES	TEST METHODS	CONDITIONS	UNITS	RESULTS Grease 1	RESULTS Grease 2
P0	ASTM D217	--	1/10 mm	343	322
P60	ASTM D217	--	1/10 mm	346	330
Dropping point	ASTM D2265	--	°C	>300	>300
Oil separation	ASTM D6184	30 h - 200°C	%m	6.9	5.9
Evaporation	ASTM D2595	22 h - 200°C	%m	4.2	4.6

Figure 16. Basic bench test results on ester based greases

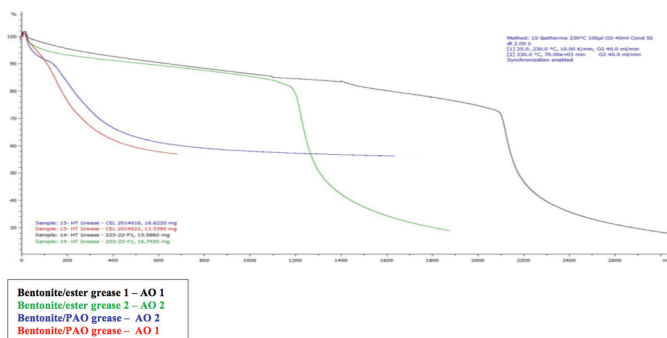


Figure 17. TGA, 230C, O₂

3.5 Combination of high performance and low environmental impact

Hydraulics is a specific area where future fluids will have to be:

- more resistant to rising temperatures, as a result of increased power density;
- robust anti-wear fluids, to protect pumps and deliver energy efficiency;
- cleaner products, to facilitate filtration on finer filters;
- more consistent in viscosity over temperature for improved energy efficiency;
- fire resistant, as liability in case of fire is a growing concern;
- environmentally friendly.

Suitably selected neopolyol esters do provide high performance as base fluids for hydraulic oils. They show high Viscosity Indices, without using any polymer, thus ensuring excellent shear stability

and hydraulic efficiency. They are resistant to oxidation and provide extended lifetime as well as superior cleanliness. They are excellent lubricity fluids, as demonstrated by wear test results on vane pumps. They also show high flash points, for improved fire safety. Seal compatibility and water or air separation are of a very good level. Finally, they show high levels of biodegradability and renewability, thus complying with European Ecolabel or Vessel General Permit requirements (Figure 18).

ISO VG 46 – ISO 15380 – European Ecolabel compliant hydraulic fluid			
Composition	Saturated neopolyol ester : 98.746%		Complex ester : 99.095%
	Additives : 1.250%		Additives : 0.900%
	Anti-foam : 0.004%		Anti-foam : 0.005%
Kinematic Viscosity, mm2/s			
100°C	ISO 3104	7.9	8.31
40°C		45.6	45.0
Flash Point, °C	ISO 2592	281	260
Dry TOST, hours	ISO 4263-3	>7000	>2100
Van Pump wear (V104C)			
Cam ring, mg	ISO 20763	2.0	4.1
Vanes, mg		12.3	1.1
Biodegradability	OECD 301B	>60%	>60%
Renewable carbon content	-	>50%	>50%

Figure 18. European Ecolabel compliant hydraulic fluid

Neopolyol ester based hydraulic fluids are high performance lubricants that also demonstrate excellent environmental profile.

In a different area, specific high viscosity synthetic esters (up to ISO VG 1,000) do exhibit high biodegradability and renewability levels, which make them excellent fluids for the formulation of greases meeting environmental standards like the European Ecolabel or the Vessel General Permit. In particular, they may be used to formulate marine greases used for bearings, wire ropes, and open gears thanks to their high degree of tackiness and excellent overall performance level.

Conclusion

It appears that synthetic esters have a lot more to offer than what they have been traditionally used for, and the current market drivers will most probably unveil unexpected, sometimes unknown, added benefits of these base fluids, and promote their use in modern, high performance lubricating applications.

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LINKS
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