The Development of CARILON EP Polymers for Commercial Applications. I

Exterior Automotive Applications

E. R. George, J. H. Coker, Jr.

Technical Progress Report **WRC 12–88**
Project No. 62182

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Shell Development Company
A DIVISION OF SHELL OIL COMPANY

Westhollow Research Center
Houston, Texas

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PRINTED: **April 1988**

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REFERENCES: LR–18148, pp. 1-199
Based on work through November 1987

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ABSTRACT

The viability of using CARILON EP Polymer compounds for automotive body panels was demonstrated. Neat CARILON EP polymers were modified via reinforcement and polymer blending to achieve a good property set suitable for automotive body panels. Compounding and injection molding conditions were established and subsequently Ford Econoline van and Taurus sedan fenders were painted under typical automotive paint conditions and passed all Ford and GM paint specifications. Further development is needed to increase the melt processing window and to improve low temperature impact resistance.

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by

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SUMMARY

This report describes the development of CARILON EP polymer, an engineering thermoplastic, for automotive body panels. CARILON EP polymers are terpolymers synthesized via the addition polymerization of carbon monoxide, ethylene, and some propylene. The amount of propylene used and the degree of polymerization (molecular weight) are the two most important variables which affect the properties of neat CARILON EP polymers. Systems may be tailored for specific applications via alloying, reinforcement, and process optimization. While this investigation targets automotive body panels, the results apply generally to electrical, packaging, and industrial applications.

Plastics are rapidly replacing exterior body panels traditionally cast from steel. Plastics are particularly feasible when less than 200,000 vehicles of a particular model are produced due to the expensive tooling costs for steel. In the last decade a broad range of engineering and specialty plastics were developed for exterior body panels. These materials must meet manufacturing, engineering, and market objectives. The design of the part should be integrated with the material property set at an early stage of development. This investigation concentrated on the tailoring of CARILON EP polymer compounds to meet material requirements. The data base necessary for computer aided design programs was collected and reported here.

The polymer compounds competing in the automotive body panel market include thermoplastics and thermosets. Table 1 compares the properties of these two types of polymers as related to automotive body panel applications. The thermoplastics are primarily blends of polycarbonate (PC), ABS, nylons (amorphous and aromatic), saturated polyesters, and polyphenylene oxide (PPO). Thermoplastics may be processed by injection molding which offers fast cycle time, automation, and design flexibility. Two types of thermosets are generally used:

- glass fiber filled unsaturated polyesters (processed via sheet molding compound, SMC)
- polyurethanes and polyureas (processed by reaction injection molding, RIM)

RIM polyurethane systems often use flake glass fillers as opposed to fibrous reinforcement.

Exterior body panels are classified as either horizontal or vertical. Horizontal body panels include hoods, roofs, and trunk lids. Vertical body panels include fenders, doors, fascia, lift gates, closure panels, and rear quarters. This report is concerned with the development of a vertical body panel, particularly a front fender. The requirements for horizontal body panels are almost identical except that much higher strength and modulus is necessary and the parts are larger. SMC can be molded into large parts exhibiting the required mechanical properties for horizontal body panels. SMC is expected to dominate the horizontal body panel market made from polymers through 1992. Injection molded thermoplastics are expected to capture 20% of the front fender market by 1992. Thus, front fenders are a valuable, high volume application for CARILON polymers.

The success of thermoplastics in the automotive market depend primarily upon meeting product specifications with the advantage of fast cycle times, design flexibility, and weight savings compared to steel and reinforced thermosets. Thermal expansion, heat sag, warpage, shrinkage, and creep can often prevent the use of thermoplastics in many applications. Body panels must be exposed to temperatures up to 410°F during on-line priming and painting. Off-line painting temperatures (ex. Fiero) currently range from 250 to 275°F. Reinforcement and blending can be used to overcome the inherent limitations of CARILON EP polymers in automotive applications.

RESULTS AND DISCUSSION

PROPERTIES OF NEAT CARILON EP POLYMERS

The majority of the CARILON EP polymer nibs provided by the MDU exhibit a melting point from 215°C to 225°C and an LVN of 1.4 to 2.0. Table 2 lists the properties of injection molded test specimens with the range of data due to melting point and molecular weight differences. Mechanical properties were reported for dry as-molded injection molded test specimens. The equilibrium water absorption is ~1.0%w which results in a lower modulus and increased impact resistance. CARILON EP polymer is an addition polymer and the presence of water during compounding and molding will not reduce molecular weight as would be the case with polyamides (nylon) or polyesters (PET and PBT). This is a definite advantage for CARILON polymers versus condensation type polymers.

CARILON EP polymers exhibit an increase in impact resistance with increasing LVN (i.e., molecular weight). At an LVN of ~1.9 there is a transition where the notched izod impact resistance increases to ~10 ft lb/in. from ~3 ft lb/in. However, melt viscosity increases exponentially with increasing molecular weight ($\eta \propto M^{3.4}$) and the cost of producing higher LVN polymer also increases due to longer reaction time. Thus, there is a trade-off between melt processability and cost with the maximum impact resistant polymer.

MEETING AUTOMOTIVE BODY PANEL REQUIREMENTS VIA COMPOUNDING

Neat CARILON EP polymers exhibit an excellent combination of physical properties for a polymer projected to cost <$1.50/lb. Table 3 lists the generic requirements for vertical automotive body panels. While CARILON EP polymers exhibit a good property set, the polymer must be modified to meet the requirements for automotive body panels. Reinforcement, alloying, and molecular weight control were used to tailor CARILON EP polymer compounds to meet the specifications of automotive body panels. Table 4 lists the key properties which must be controlled with the desired direction of the property value. The elimination of propylene in CARILON polymers increases modulus and heat deflection temperature, two desirable directions for property value.

REINFORCEMENT WITH CHOPPED GLASS FIBERS

CARILON EP polymers were blended with OCF chopped fiberglass 457 and 492 on a Haake 30 mm twin screw extruder. The original length of the chopped fibers was 3/16 inch and 1/8 inch, respectively. OCF 457 and 492 glasses are sized with coupling agents designed for interfacial adhesion with polypropylene and polyesters, respectively.

Figure 1 illustrates that the flex modulus increases with increasing fiberglass content but depends upon the type of glass and initial starting modulus of the neat resin (i.e., propylene content). The combination of the higher modulus polymer and OCF 492 resulted in the best properties including improved flex strength, heat deflection temperature, and mold shrinkage.

THE EFFECT OF BLENDING AN ETHYLENE—ACRYLIC ACID COPOLYMER WITH CARILON EP POLYMERS

Compounding studies with available grades of CARILON EP polymer showed that 10%w OCF 492 fiberglass yield a modulus and strength meeting specifications for exterior automotive vertical body panels. The addition of 5%w Primacor 1430 (an ethylene-acrylic acid copolymer) improved the impact resistance, modulus, and strength of the reinforced or neat CARILON EP polymer systems. Secondly, the Primacor served as a processing aid and required lower injection pressures and enhanced the crystallizability of the semi-crystalline CARILON EP polymer.

The positive effect of utilizing Primacor 1430 in CARILON EP polymers was demonstrated with batches 86/005, 86/006, 86/007, 87/006, 87/020, and 87/025. The increase in impact resistance was observed in all batches where LVN was less than 1.8. Modulus and strength were improved in all cases. Table 5 shows the data for batch 86/007 and is representative of all batches. The combination of using fiberglass and Primacor was particularly useful since this system meets most requirements for automotive vertical body panels.

Lower injection pressures and times are required for molding the CARILON polymer systems containing 5%w Primacor 1430. Subsequently, lower clamp tonnage and smaller, lower cost injection molders may be employed for molding operations. Blends of CARILON EP polymer with Primacor 1430 show enhanced crystallizability in the DSC protocol test. This can be attributed to a nucleation effect and/or improved melt stability.

Novel and proprietary compounds of CARILON EP polymers, fiberglass reinforcement, and an ethylene-acrylic acid copolymer were identified. Three patent applications were filed concerning these compounds and their utility in automotive applications.

PROCESS OPTIMIZATION

Processing conditions must be controlled to minimize degradation and to produce the desired morphology in the finished part. Compounding and injection molding conditions were established to produce viable automotive body panels with CARILON polymers. The most important variables in either process are time and temperature.

All compounding was performed on a 30 mm twin screw corotating extruder. All large compounding runs were done at Paragon Development. It was most important to control the melt temperature at the die less than 260°C. One mixing zone was used located where the polymer first becomes molten in stage 2. Stage 3 was a transport zone and stage 4 adjacent to the die was equipped with a vacuum for devolatilization. Ionol was removed from all batches. In all runs Ethanox 330 or Irganox MD 1024 was added at 0.5%w for additional stabilization. Primacor was used as a processing aid and melt stabilizer.

Cycle time and clamp tonnage were the key variables for injection molding. Minimum cycle time is required to reduce the residence time of the polymer in the barrel. By keeping the ratio of the machine capacity to the shot size at a minimum, injection molding of CARILON polymers can be readily achieved. Total residence time should never exceed 10 minutes.

CARILON EP polymer compounds were molded at clamp tonnages of 2.0–2.5 tons/in^2 of part surface area. This represents a low clamp tonnage for engineering thermoplastics and verified that the injection-molding of large parts on commercial equipment is feasible. The practical significance of this finding is that front fenders for the typical automobile may be molded on a 3000 ton or less injection molding machine.

PROPERTIES OF CARILON EP POLYMER AUTOMOTIVE COMPOUNDS

Thermoplastics have begun to penetrate the automotive market in exterior automotive body panels. Noryl GTX and Bexloy C are examples of thermoplastic blends targeted for automotive applications from GE and Dupont, respectively. Noryl GTX is an impact modified PPO/nylon blend now used for the front fender on the Buick Le Sabre. Bexloy C, an amorphous aromatic nylon developed by Dupont is now used for the lower rear quarter panel of the Pontiac Fiero. These two polymer systems are expected to be the key competitors for CARILON polymer in the automotive body panel market.

Two CARILON polymer compounds were prepared for molding automotive body panels (Table 6). One compound consisted of a low LVN (~1.5), unreinforced material which was relatively easy to process. The second compound contained a higher LVN (~1.9) base polymer reinforced with 8%w fiberglass. This compound was more difficult to process but good parts were produced of Ford Econoline and Taurus fenders.

Table 7 compares the properties of the two CARILON EP compounds with Noryl GTX, Bexloy C and also to the CPC (Chevrolet Pontiac Canada Group) specification for vertical, off-line painted body panels. The CARILON EP polymer compounds met all specifications except CLTE and low temperature impact resistance. The glass-filled CARILON polymer compound exhibits an excellent balance of stiffness and impact resistance due to reinforcement and the use of a high LVN base polymer. The reinforcement significantly improved heat deflection temperature (HDT) and thermal expansion coefficient.

Both CARILON EP polymer compounds compare favorably to Noryl GTX and Bexloy C. The HDT is lower because the CARILON polymer has a much lower melting point than nylon. The use of reinforcement combined with higher melting point base polymer can significantly increase HDT. CARILON EP polymers require low temperature impact modification. This problem will be studied in 1Q 1988. CARILON EP polymer compounds absorb lower amounts of moisture than mylon based polymer systems, therefore, dimensional tolerance is superior. Secondly, CARILON polymers are not subject to hydrolysis in the presence of H_2O.

MOLDING TRIALS

Table 8 outlines the various parts which were molded during 1987 at separate molding trials. Smaller parts were molded in the 1Q and 2Q in order to prepare for molding the larger fenders in the 3Q and 4Q. This report concentrates on the molding of the two fenders, however, the window cranks and headlight bezzles are viable applications for CARILON polymers.

Ford Econoline and Taurus front fenders were molded successfully at Allmand Associates on a 3000 ton, 412 ounce Kraus Maffei injection molder with CARILON EP polymer compounds. The 412 ounce barrel holds ~30.1 lbs of CARILON EP polymer compound and the total shot weight was ~7.0 lbs. This resulted in a total residence time of ~6.5 minutes assuming no interruptions in the molding process. Table 9 lists typical molding parameters for the two CARILON EP polymer compouunds (Table 6).

The tool used for the Econoline fender was Kerksite and contained two hot drops leading to eight pingates. The tool was old and had many surface imperfections as well as manual inserts which increased the clamp open time. Compound 1 exhibited good melt stability throughout the molding trail while the fiberglass reinforced compound 2 showed signs of degradation and was not run continuously.

A superior steel tool was used for molding the Taurus front fender which also had a proper gate design (fan gate) and placement along with a smoother class A surface mold. Compound 2 molded well in the steel Taurus tool and was run continuously for ~2 hours producing >50 good parts. The temperatures were lowered ~15° in all zones and at the die from those used during the Econoline fender trail. The use of a good tool combined with faster cycle times demonstrated the feasibility of producing large automotive parts continuously with CARILON EP polymer compounds.

PAINTABILITY

Headlight bezzles and Ford Econoline fenders were primed and topcoated according to both on-line and off-line paint conditions. The parts passed all GM and Ford paint performance tests and Florida exposure tests were started. Table 10 contains the various combinations of primer-topcoat systems and the paint schedule. The first three primers are standard conductive primers for off-line primer conditions. These conductive primers must first be applied for the ELPO process (electrostatic deposition) to be effective on plastic parts. Primed parts were topcoated with and without E coat. Table 11 lists the GM test specifications for paint performance and all parts passed. Preliminary results for the Florida exposure test will be reported 2Q 1988.

CONCLUSIONS

- CARILON EP polymer compounds exhibit properties characteristics of *Engineering Thermoplastics*

- Injection moldability is exceptional for an Engineering Thermoplastic
- CARILON EP polymer compounds are *viable* for vertical body panel applications
- Front fenders injection molded from Engineering Thermoplastics are projected to grow to a large *volume* market by 1992
- The *value* of CARILON EP polymer compounds is expected to be $1.50/lb ± $0.30/lb

ACKNOWLEDGEMENT AND REFERENCE

This work would not have been possible without the help of many discussions and the use of their personal files with:

D. S. Brath

R. L. Danforth

P. S. Byrd

R. G. Lutz

W. P. Gergen

G. B. Klingensmith

D. L. Handlin

R. Q. Klutz

W. H. Korcz

E. Smutny

W. P. Rothwell

Many of their ideas lead the way for automotive applications and their teamwork was appeciated.

Table 1. Comparison of Thermosets versus Thermoplastics in Automotive Body Panel Applications

Thermosetting Resins		Thermoplastic Resins	
Advantages	Disadvantages	Advantages	Disadvantages
Class A surface (low profile only)	Low first run capability	Class A surface	Low mechanical properties (i.e., modulus)
Design flexibility	Not conducive to automation	Design flexibility	High molding pressure
Weight savings vs steel	High density vs thermoplastics (30–40%)	Weight savings vs steel and FRP	High material cost
Excellent mechanical properties (i.e., modulus)	Reusability	Fast cycle time	Chemical resistance
Excellent dimensional control at elevated temperatures (low profile only)	Long cycle times	Highly automated process	Glass fiber soluble (aspect ratio reduced)
Low material cost		High first run capability	Poor dimensional control at elevated temperatures
Glass fiber reactive (retains aspect ratio)		Reusable	One process
		Corrosion resistance	
		Shelf life	

Table 2. General Property Set of Neat CARILON EP Poymers

Flex Modulus	200,000 – 240,000 psi (R.T.) 100,000 – 140,000 (158°F)
Tensile Strength	6,500 – 7,500 psi
Elongation to Break	100 – 200%
Notched Izod Impact	3 – 10 ft lb/in. (R.T.) 1 – 2 ft lb/in. (–20°F)
CLTE	$6 - 8 \times 10^{-5}$ in./in./°F
Heat Deflection Temperature	200 – 250°F
Moisture Absorption	0.5 – 1.0%w
Humidity Growth	0.3 – 0.4%
Heat Sag (375°F 30 min)	0.1 – 0.3
Gardner Impact	100 – 200 ft lb (R.T.) 15 – 30 ft lb (–20°F)

Table 3. Generic Requirements for Automotive Vertical Body Panels

Property	Requirement
Flex Modulus	300,000 psi (R.T.) 150,000 psi (158°F)
Tensile Strength	4,000 psi
Elongation to Break	20%
Notched Izod Impact	2.5 – 5.0 ft lb/in. (–20°F)
CLTE	$1 - 4 \times 10^{-5}$ in./in./°F
Heat Deflection Temperature	300°F
Humidity Growth	0.2 – 0.3%
Heat Sag (375°F 30 min)	0.4 in.

Table 4. Properties of CARILON EP Polymer Requiring Modification for Use As Automotive Body Panels

Property	Technique	Direction
Flex Modulus	Fillers E vs EP	Increase
Impact Resistance		
(R.T.)	Higher LVN	Increase
(–20°F)	Impact Modifier	Increase
CLTE	Fillers	Decrease
Warpage	Symetrical Fillers (ex. MICA)	Decrease
Heat Deflection Temperature	Fillers E vs EP	Increase
Humidity Growth	Fillers (hydrophobic)	Decrease

Table 5. Mechanical Properties of CARILON EP Polymer Compounds

Sample	Flex Modulus (psi)	Flex Strength (psi)	Notched Izod (R.T.) (ft lb/in.)
86/007 (control)	206,000	7,200	4.2
5–1430–86/007[1]	212,000	7,500	5.3
10–492–007[2]	304,000	10,300	2.1
5–1430–10–492–007[3]	360,000	8,900	3.1

[1]86/007 + 5% Primacor 1430.
[2]86/007 + 10% OCF 492 fiberglass.
[3]86/007 + 5% Primacor 1430 + 10% 492 fiberglass.

Table 6

Component	Function	%w
System 1		
CARILON EP 87/020, 022	base resin	92.0
Primacor 1430	impact modifier processing aid paint adhesion promotor	5.0
TiO_2/EVA black	pigment	2.5
Irganox 1024	stabilizer	0.5
System 2		
CARILON EP 87/025, 026, 027, 028	base resin	84.0
Primacor 1430	see above	5.0
OCF 492 Fiberglass	reinforcement	8.0
TiO_2/EVA black	pigment	2.5
Irganox 1024	stabilizer	0.5

Table 7. Engineering Polyketone vs Other Injection Molded Engineering Thermoplastics

Properties	Buick Fender PPO/Nylon GTX 910	Fiero QTR Panel A. Nylon Bexloy C	Engineering Polyketone		CPC[1] SPEC
			Neat	Glass	
Tensile Strength, psi	6,800	6,200	7,500	8,000	4,000
Flexural Mod, R.T., psi	250,000	250,000	245,000	361,000	225,000
Flexural Mod, 150°F, psi	160,000	150,000	—	—	145,000
Izod Impact R.T. (ft lb/in.)	4.5	13.0	4.5	4.4	—
Izod Impact, -20°F, (ft lb/in.)	2.5	5.5	1.6	1.6	—
HDT, @ 264 psi, °F	290	275	230	250	—
Heat Sag, 1 hr (250°F)	0.1	0.04	0.03	0.04	0.2
(325°F)	0.2	2.0	0.09	0.09	—
(375°F)	0.5	—	0.5	0.5	—
CTE x10^{-5} in./in./°F	5.0	5.0	7.0	5.0	4.0
Humidity, % Growth	0.45	1.2	0.3	0.3	0.3
Specific Gravity	1.1	1.1	1.2	1.25	—
Elongation at break, %	—	—	104	96	25

[1]Specification for vertical, exterior, off-line painted body panels.

Table 8. Molding Trials in 1987 for CARILON EP Polymer Compounds

1st Quarter

- Motor Housings
- Black & Decker Blender Bottom

2nd Quarter

- Headlight Bezzles

3rd Quarter

- Ford Econoline Fender
- Volkswagon Window Cranks

4th Quarter

- Ford Taurus Fender

Table 9. Molding Parameters

	Compound 1	Compound 2
Barrell Temperature		
Rear Zone	470°F	490°F
Zone 2	480°F	500°F
Zone 3	500°F	510°F
Nozzle	500°F	520°F
Clamp Tonnage	2000 tons	2200 tons
Injection	5 sec, 1501 psi	5 sec, 1696 psi
Hold	10 sec, 603 psi	10 sec, 602 psi
Clamp Close Time	40.5 sec	40.5 sec
Clamp Open	40–50 sec	40–50 sec
Cycle Time	80–90 sec	80–90 sec

Table 10. Part Painting Schedule

Part Preparation
Seven Stage Power Wash

	Bake Temperature/Time
Priming System Conductive	
PPG MCP 9500	350°F/30 min
SO BP 9245	350°F/30 min
AKZO 11BME 42027	280°F/30 min
E-COAT/ELPO	385°F/22 min
E-COATt/ELPO Simulated	400°F/60 min
Primer/Surfacer	
PPG DPX 1715	280°F/30 min
Top Coat Systems	
PPG UBC/URC	270°F/30 min
PPG HUBC/URC	270°F/30 min
PPG DHT	260°F/35 min
PPG DCT/DCT	260°F/35 min

Table 11. Paint Performance Testing
GM 4350-M, Class AO

Adhesion (GM 9071-P)	Pass
Water Immersion (GM 4466P)	Pass
Humidity (GM 4465P)	Pass
Cure Xylene (8 Rubs)	Pass
Thermal Shock (Ford FLTM-B1-7-5)	Pass
Flordia Exposure in Progress	

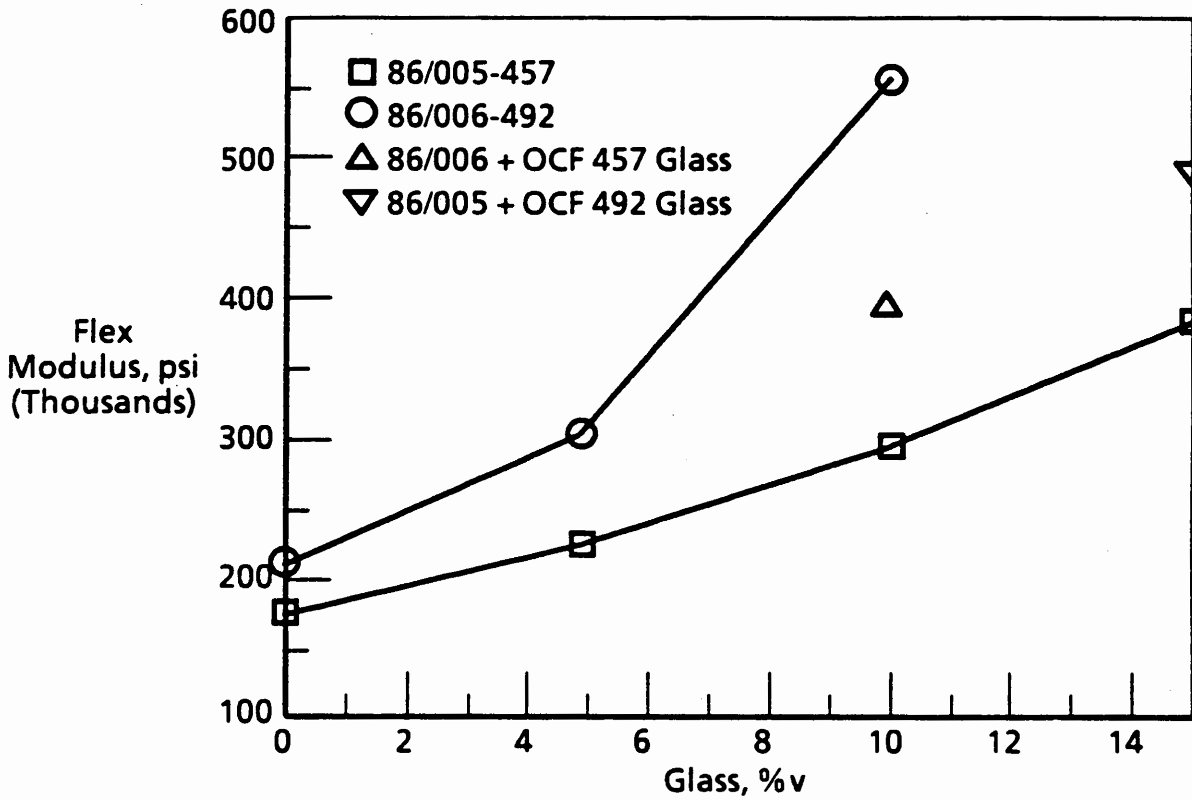

Figure 1. CARILON EP Polymer-Glass Blends
86/006,005 OCF 492,457

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