Core preservation packaging materials and techniques, their advantages and limitations

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Abstract. Core preservation is a crucial step in the evaluation and efficient production of hydrocarbon reserves. By maintaining the rock in the same physical, chemical and fluid saturation condition it arrives at surface, assuming no permanent downhole alteration, the probability of laboratory technicians delivering accurate core analysis improves. The industry employs a variety of materials (mylar bags, cling film, wax, aluminum foil, containment vessels) and techniques (inert gases, vacuum sealing, multiple layer packaging, refrigeration, oxygen scavengers) to preserve core. Ideally the core packaging prevents moisture loss and oxidation, does not deteriorate with time, is chemically inert to hydrocarbon and oilfield brine exposure, and prevents biological growth.

Plastic cling film is an easy to apply core preservation material. Modern cling films dramatically slow moisture loss but are significantly less effective at decreasing oxygen transmission than earlier chemical formulations. Cling film may react with the reservoir crude depending on the crude's chemistry.

Aluminum foil is another material commonly utilized for core preservation. The metal is a barrier to the transmission of water vapor and oxygen. However, even when tightly wrapped around the core, gas leakage paths exist along the seams of the packaging.

Melted waxes are popular. They cushion the core against mechanical damage and slow moisture loss. However, they are not effective at preventing rock oxidation.

Air tight Mylar[TM] laminate bags flushed by a chemically inert gas (nitrogen, argon, helium) and a vacuum drawn prior to heat sealing provide an excellent option for core preservation. Oxygen scavengers may be included in the package to bind any free oxygen remaining in the annual space. Rough handling and non-cushioned core transportation may puncture the bags rendering the preservation ineffective.

Air tight sealed metal, plastic or glass cylinders containing core immersed in deoxygenated brine, native crude or nonpolarizing oil is an excellent technique though not common due to the expense of the vessels. Oil immersion is the most suitable preservation technique for shale core mechanical studies where any desiccation negatively affects the measurements.

Maintaining a 4 to 10 deg. C temperature and 45 to 55% air relative humidity core storage environment slows chemical reactions, moisture evaporation and biological growths. Studies in the literature indicates core preservation life is limited to two to three years.

This paper reviews the advantages and limitations of the various core preservation material properties and techniques followed by the authors recommendations for effective preservation.

Introduction

This document provides the reader with information on the techniques and materials used by the oil and gas industry to preserve rock samples obtained from the subsurface during drilling and / or wireline operations. The samples provide valuable information about the physical and chemical properties of the rock and any fluids contained within the rock's pore space. Preserving these core samples in their original state is crucial for accurate analyses and interpretation of the data they provide for hydrocarbon resource estimation, rock mechanical properties and special core analyses for reservoir modelling. Without proper preservation the cores may undergo physical and chemical changes, altering their properties, making the samples less useful for research and analyses.

Oil and Gas companies employ various techniques to prevent core alteration including low invasion core heads in conjunction with non-wettability altering, sized particle coring muds, controlled speed rock extraction from the subsurface, minimizing exposure to the atmosphere on surface, encapsulation of the rock samples in preservation materials and storage in a temperature-humidity controlled environment. Each technique and material used has advantages and disadvantages. No preservation procedure

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halts the transfer of gases and water vapour between the rock material and the atmosphere. It can only slow the process. Nor can preservation prevent wettability alteration due to the crude oil's chemistry (asphaltic / paraffinic) and the effects of pressure and temperature loss[6]. The food and pharmaceutical industries with similar preservation goals have for decades applied advanced product encapsulation materials and procedures. A preservation expiry date is assigned to the product unlike the Oil & Gas industry. This paper focuses on the rock packaging procedures and materials used to prevent deterioration of rock samples once they reach surface and suggests a time limit on the effectiveness of these procedures. Recommendations contained within seek to extend the length of time a rock may be considered preserved.

Barrier Materials for Long Term Core Preservation

Core Preservation Objectives
The objectives of core preservation are:

1. Maintain the arrive on surface core condition for an extended storage time period (at least 3 years).
2. No wettability change (no oxidation and moisture loss).
3. No liquid loss (saturation change) due to evaporation from the sample.
4. No chemical reactions between the packaging material and core fluid contents.
5. Prevent / limit migration of coring fluids into the rock (for plugs drilled on surface) and inhibit further contact with air.

Core preservation procedures were developed pre 1990 based on materials used for food and pharmaceutical product preservation. Today, some of the materials are no longer in mass production i.e. Barex™ or the chemical formula has changed i.e. pre 2004 Saran™ Wrap versus post 2004 Saran™ Wrap.

Barrier Material Requirements
Barrier material requirements for long term core preservation are extensive.

1. Chemical resistant to a variety of crude oils, hydrocarbon gases and associated gases such as H_2S, CO_2 and high salinity brines.
2. Does not absorb liquids from the core when in direct contact.
3. Very low gas permeability especially for oxygen.
4. Very low water vapour (WV) permeability.
5. Low to no Gas / WV permeability sensitivity to relative humidity levels: i.e. little to no Gas / WV permeability change.
6. Flexible, easily formed to different sample dimensions thereby limiting air head space.
7. Scavenges oxygen.
8. Barrier properties stable under core storage temperatures (-10 deg. C to +60 deg. C).
9. Liquids remain in the sample rather than transfer to the air headspace of the package.
10. Minimizes water vapour moisture transfer from the sample and package headspace to surroundings.
11. Flex crack resistant. Does not crack when folded.
12. Not susceptible to pinholes and punctures.
13. Hermetically sealable (Note: Very low gas and water vapour material transfer properties has little medium to long term storage value unless the material is hermetically sealable.)
14. Does not degrade with time.

No single barrier material satisfies all core preservation requirements. Layers of materials with different properties are required. Common Oil & Gas industry practice is to first wrap the core sample in cling film (commonly labelled Saran™ Wrap) or Barex™ (less frequently) followed by aluminum foil and then encase the product in meltable paraffin / plastic wax. Laminated Mylar® heat sealable bags are also used to hold the raw sample or a wrap and waxed version. Primary function of the cling film or Barex™ is to isolate the aluminum wrap from contact with brine in the core and cushion it for the rock's rough surface. For this objective the film must be resistant to chemical attack from crude oil, natural gas, CO_2 and H_2S.

Plastic wrap and wax preservation materials are permeable to gases and water vapour. The food industry has databases documenting rates of oxygen / water vapour transfer and the chemical resistance of various plastic barrier film materials to chemical compounds including fuel oil, diesel and gasoline. Oxygen / water vapour barrier effectiveness of plastic flexible films is classified as Low to Very High as per **Table 1**. Reservoir crude may or may not react with plastic depending on the individual crude oil's composition. Thirty micron thick aluminum is effectively impermeable to gas, water vapour and does not react with crude oil. However, since it is folded around the core, it leaks around the edges. Aluminum corrodes on exposure to oxygen but forms a protective layer to further corrosion. Aluminum corrodes with increasing chloride concentration, temperature, and exposure time (totalmateria.com, engineeringtoolbox.com).

Table 1. Plastic Barrier Film Effectiveness Classifications

Barrier Classification	Oxygen ASTM D3985	Moisture ASTM F1249
Low	>100 cm³/m²/24hr	>100 g/m²/24hr
Medium	6-100 cm³/m²/24hr	6-100 g/m²/24hr
High	1-5 cm³/m²/24hr	1-5 g/m²/24hr
Very High	<1 cm³/m²/24hr	<1 g/m²/24hr

Source: PCI Films Consulting Ltd.

The food, pharmaceutical and conservation (museums) use multilayer barrier films. The outer layer is a strong (usually transparent) plastic with a relatively high melting point often made of polyester (Mylar™, Melinex®), nylon or polypropylene. The inner/middle layer will be a thin layer forming a gas barrier (ceramic, EVOH, PVdC, Al, SiO_2). The inside/bottom layer is typically a low density polyethelene which softens and sticks at relatively low temperatures to allow heat sealing. Additional layers increase the barrier

properties of the film. Polyester, polypropylene and polyethylene are poor gas barriers on their own. Oxygen scavenging capabilities built into specialized plastics such as Sealed Air's Cryovac® Freshness are available as heat sealable pouches. This product is an attractive package for core preservation when rock surface oxidation is a concern.

Flexible Wrapping Materials

PVdC and LDPE Composition Cling Films

Gas Permeability
Oxidation and drying of the reservoir rock sample causes wettability change and clay shrinkage (if clays are present), altering the rock and its contained fluids natural state. This makes it impossible to carry our fresh state Special Core Analysis (SCAL) and may make it difficult to clean the rock to a strongly water wet condition if a clean and restore procedure is followed for analysis. Saran[TM] Wrap is a commonly used cling film for core preservation. Dow Chemical began marketing the film in 1953 as a highly flexible food wrap. The product was originally composed of polyvinylidene chloride (PVdC). In 1997, Dow Chemical sold the trade name to S.C. Johnson [1,2]. As of 2004, Saran[TM] Wrap sold in North America and Australia is composed of Linear Low Density Polyethylene (LLDPE) or its cousin, Low Density Polyethylene (LDPE). These films have significantly higher oxygen permeability and moderately higher water vapour permeability than PVdC composition film. For core preservation PVdC film is preferable to LLDPE and LDPE composition cling films for its low oxygen and water vapour permeability.
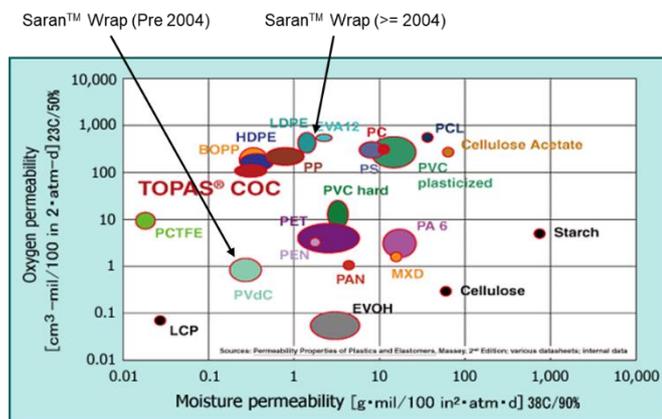

Figure 1. New SaranTM Wrap has considerably higher O$_2$ permeability than old SaranTM Wrap (figure, polyplastics.com)

Chemical Resistance
LLDPE, LDPE and PVdC films swell and soften when in contact with aromatic hydrocarbons [3,4,5]. **Figure 2** is an example of a LDPE composition cling film's condition after several years contact with an UAE Thamama 34 API crude oil. The oil left the rock sample and was absorbed into the cling film which was notably swollen and deformed. The rock sample itself was dry to the touch.

Hunt and Cobb (1988) testing the chemical resistance of PVdC cling (pre 2004 Saran[TM] Wrap) film for a core preservation program discovered it degraded (**Table 2**) in

Alaskan crude and other petroleum products in contrast to the low chemical reactivity of Barex 210[TM], a modified acrylonitrile copolymer resin (general name, polyacrylonitrile (PAN)).

Figure 2. Crude oil penetrated the LDPE cling film of this RP40[15] wrap/wax preserved sample after several years storage. The rock sample was dry to the touch.

Table 2. Barex 210[TM] and PVdC pre 2004 Original Saran[TM] Wrap Chemical Reactivity [6]

Percent Material Weight Loss After 30 Days Exposure at 37.8 deg. C		
Liquid	Barex 210[TM]	PCdC pre 2004 Saran[TM] Wrap
Heptane	1.2	3.1
Cyclohexaane	0.1	2.0
Gasoline	0.1	2.0
Benzene	1.1	2.3
Toluene	0.2	1.9
Alaskan Crude	0.3	2.3
Diesel	0.4	8.2
Oil Drill Mud	0.6	1.4

Hunt and Cobb, 1988

Barex 210[TM] Film

Gas Permeability
Barex 210[TM] resin film is less permeable to oxygen than PVdC cling film but has significantly higher permeability to water vapour (**Table 3**). The film's stiffness makes it significantly more difficult to work with than cling films.

Table 3. Barex 210[TM] Barrier Film Effectiveness[7]

Material	Oxygen (cm^3 x mm / m^2 x D x atm)	Water Vapour (WV) (g x mm / m^2 x D x atm)
PVdC	0.43 – 0.78	98
Barex 210[TM]	0.35	784

Massey, L., 2003. Orig. formula Saran[TM] Wrap (WV: 37 deg.C, 90% Rel. Humidity). Barex 210[TM] (Gas: 23 deg.C, 0% Rel. Humidity. WV: 23 deg.C, 100% Rel. Humidity)

Chemical Resistance

Chemical Resistance
Barex 210™ has excellent chemical resistance to petroleum products and crude oil (**Table 2**). The product however is difficult to source. Its main U.S. producer halted production in 2015 after losing the food industry to less expensive, less capable products. Barex 210™ remains available from boutique chemical companies. A flexible replacement film for Barex is Teflon® perfluorinated ethylene propylene (FEP) or Teflon® perfluoroalkoxy (PFA). These films are highly permeable to oxygen, moderately permeable to water vapour and highly resistant to hydrocarbon chemical attack (www.calpaclab.com/chemical-compatibility-charts).

Laminate Barrier Films

Gas Permeability
Laminates combine the best properties of multiple materials into a single film with very low oxygen and water vapour transmission rates (**Table 4**). The International Ocean Drilling Program (IODP) uses a LDPE/MDPE/EVA/EVOH multilayer heat sealable composite (BDF-2001), a product of Cryovac Sealed Air Corporation[8] or Mitsubishi Gas Chemical Company ESCAL™-Type K[9], a heat sealable layered OPP/Ceramic(SiOx)PVAL/LLDPE film for its core preservation. Type K means an oxygen (but not moisture) scavenger agent is placed inside the packaging. Vaporized SiOx present as an ultrathin, 40 to 80 nanometer layer, fills in the porous holes present in plastics, decreasing their gas permeability. BDF-2100 acquires its very low oxygen permeability from the internal EOH layer.

Table 4. Laminate Film Barrier Effectiveness Compared to LDPE

Material	Thickness (mil)	Oxygen (cc/m²/D)	Water Vapour (g/100 in²/D)
+LDPE	0.5	400 - 1000	1 - 3
*BDF-2100	0.75	5.0	1
*BDF-2100	1.0	4.0	0.75
++ESCAL	4.4	0.05	0.01

Rumford, P., 2007, +Glad™ Wrap, *Cryovac Sealed Air Corp.
++Mitsubishi Gas Chemical Company
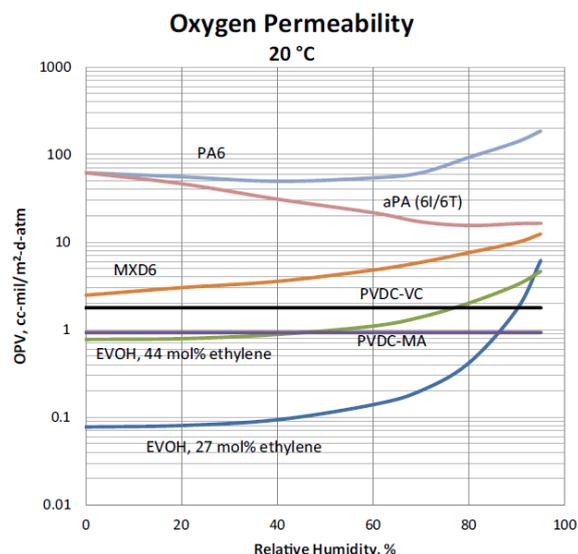

Oxygen Permeability
20 °C

Figure 3. EVOH oxygen permeability increases dramatically above 60% relative humidity[10].

EOH has very low oxygen permeability compared to LDPE, MDPE and EVA but is sensitive to relative humidity (RH). Oxygen permeability rises dramatically above 60% RH (**Figure 3**). The EOH is protected from moisture contact by plastic layers above and below. Surface scratches are a weakness of plastic laminates. Scratches penetrating one layer exposes another layer, compromising the integrity of the packaging.

Chemical Resistance
The chemical resistance of BDF-2100 and ESCAL™ was not discovered in the literature but the resistance of their individual layers to petroleum is available from various sources (**Tables 5 & 6**). The Ocean Drilling Program is not targeting hydrocarbon reservoirs, so is not concerned with hydrocarbon resistance.

Table 5. BDF-2001 Individual Layers Chemical Resistance

	MDPE / HDPE* 20&60° C	LLDPE / LDPE* 20&60° C	EVA* 20&60° C	EVOH+ (temp not stated)
Crude Oil	R & L	R & L	L & N	R
Natural Gas	R & --	R & --	L & N	---
Gasoline	R & L	L & N	---	R
Kerosene	R & L	L & N	L & N	R

*ENI, +polymerdatabase.com & kuraray.com
All films exhibit decreased resistance at increased temperature
    R = Resistant
    L = Limited Resistance
    N = Not Resistant

Table 6. ESCAL™ Individual Layers Chemical Resistance

	OPP	(SiOx)PVAL Middle Layer	LLDPE
Diesel	R	R	R
Gasoline	L	R	R
Kerosene	R	R	L

Source: Plastics Europe, Distrupol, Prinsco, Houstonpolytank,Sasol
All films exhibit decreased resistance at increased temperature
    R = Resistant
    L = Limited Resistance
    N = Not Resistant

Aluminum Foil

Gas Permeability
Aluminum foil is an excellent barrier with effectively zero water vapour and gas permeability. However, because it is folded, the foil edges do not form a continuous seal. This is a major weakness.

Chemical Resistance
Aluminum foil exposed to oxygen corrodes, but then forms a protective chemical layer preventing further oxidation. The

protective film forms only if the moisture pH is between 6 and 9 (alumeco.com). Al is amphoteric. When placed in contact with a low or high pH (<6 or >9) liquid (a drill mud may have a pH>9), Al disintegrates. The higher or lower the pH, the faster the reaction.

Aluminum deteriorates when in contact with high salinity brine. If salty water enters the crevice of overlapping sheets, a cathode / anode configuration occurs. In the presence of air, oxygen is consumed resulting in Al (**Figure 4**) dissolution and reprecipitation (totalmateria.com). Hunt and Cobb (1988)[6] observed upon opening, many of BP's preserved core samples suffered from degraded aluminum. In severe cases, the aluminum sheet was reduced to powder. A primary purpose of the first layer cling film is to protect the Al wrap from contact with corrosive brines. **Figure 5** shows an example of degraded aluminum wrap.
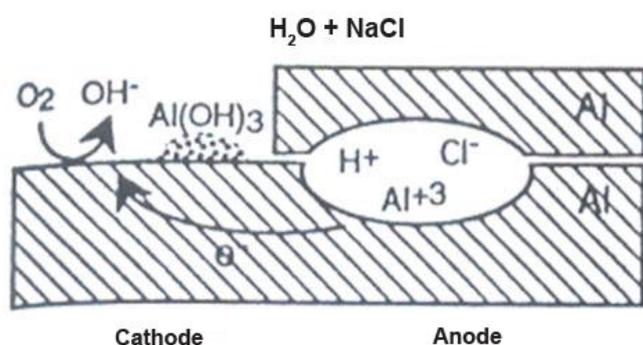

Figure 4. Crevice corrosion in a brine environment. If the crevice becomes deaerated, and the oxygen reduction reaction occurs outside of the crevice mouth. Under these conditions, the crevice becomes more acidic, and corrosion occurs at an increasing rate (totalmateria.com, 2008).

Figure 5. Degraded aluminum wrap from a UAE wax preserved core plug sample.

Thermo-Plastic, Plastic-Paraffin and Paraffin Waxes

Meltable thermo-plastic / plastic-paraffin mixtures (often referred to as wax) and paraffin waxes are widely used for the outer layer of core preservation. They provide a degree of core mechanical protection. Various wax seal products are available commercially (**Table 7**).

The effectiveness of a wax's fluid retention and mechanical protection are dependent on the product used and procedures followed[11]. Evaluations of wax preservation concluded the material does not deliver an impermeable barrier between the core and atmosphere resulting in ingress of oxygen and loss of pore fluids[6,12.13,14]. Garcia (2007) concluded in a three commercial wax weight loss comparison, the primary barrier to fluid loss was the aluminum/PVdC wrap barrier rather than the wax outer covering, a conclusion also reached by Auman (1989) and Bajsarowicz (1993). Hunt and Cobb's (1988) warehouse core samples lost up to 80% of their original water content over a two year period. Auman (1989) recorded significant water saturation reduction for core wrapped in wax, Al and cling film over a 5 year period (**Table 8**). ADNOC Offshore whole core samples when opened were dry after 5 years of storage. API RP 40[15] does not provide recommendations on the type of meltable wax to apply, the storage environment or maximum acceptable storage time (preservation expiry date).

Table 7. Commercial Core Preservation Waxes

Group	Label	Type	Softening Temp. deg. C	Melt Temp. deg. C
Plastics	B-60[1]	Cellulose acetate butyrate	82	177
	CoreSeal[2]	Thermo-plastic	132	150
	Ergo Seal 3[3]	Plastic & Paraffin	140	160
	Protecta-cote[3]	Plastic	105	130
	Type IV K-25[4]	Thermo-plastic	75	121
Paraffin	GeoSeal[5]	Paraffin	75	85
	SebaCote HDC1[3]	Paraffin	65	85

[1] Evans Coating
[2] Core Laboratories
[3] Sebca Dev.
[4] Evans Coating LLC
[5] GeoFactory

Table 8. Weight / Water Loss Over a 5 Year Period
(Wax, Al Foil, Cling Film)[12]

Sample #	Air Perm. (mD)	Porosity (%)	1977 Water Sat. (%)	1982 Water Sat. (%)
1	2.5	11.2	15	3
2	13.0	14.2	17	3
3	0.083	4.6	11	8
4	52.0	13.1	22	3
5	13.0	7.3	24	3
6	0.85	10.3	11	4
7	9.4	9.1	14	3

Auman, J.B. 1989

There is a scarcity of data in the literature on the gas transmission properties of meltable plastics and waxes. Bajsarowicz (1992) as part of an internal BP study on core preservation found high gas transmission rates for the two wax / plastic materials tested.

Table 9. Gas Transmission Rates of Two Wax Materials[13]

Material	Oxygen (cm^3 x mil / 100 in^2 x D x atm)	Water Vapour (g x mil / 100 in^2 x D x atm)
B-60 Wax	3015	122
Coreseal™	Too High to Measure	2-13

Bajsarowicz, C. 1992

Heat Sealable Mylar™ / ProtecCore™ Laminates

Mylar™ barrier film laminates (developed by Dupont 1994) combine the properties of several materials in 3 to 5 layers, providing superior moisture and gas retention capabilities. Mylar™ 50 XMMC3 contains 5 layers (**Figure 6**) composed of PVdC, Al, PET and Sealant. Core Laboratories ProtecCore™ six layer laminate has Barex™ as the innermost layer placed closest to the core. Barex™ protects the other plastic layers from chemically reacting with any hydrocarbons present, allowing moisture and oxygen to penetrate to the aluminum layer potentially compromising its seal. The next layer is biaxial nylon for strength and flexibility. Aluminum foil, two layers of low density polyethylene (LDPE) and a layer of polyester for strength follow. Because of aluminum layer present in Mylar™ / ProtecCore™ laminates, they have extremely low oxygen and water vapour transmission rates (**Table 10**).
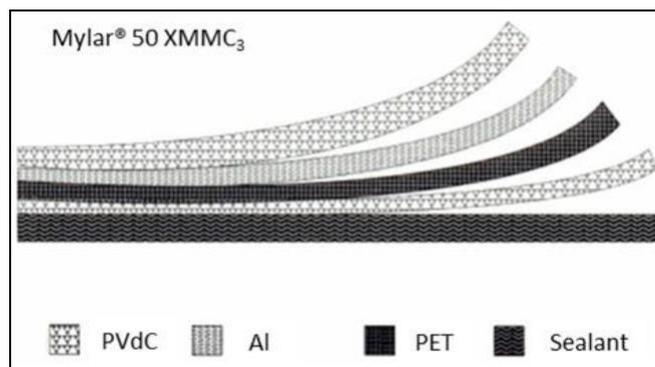

Figure 6. Mylar™ barrier film laminate construction[16].

Table 10. ProtecCore™ Oxygen and WV Transmission Rates

Material	Oxygen (cm^3 x 100 in^2 / D) at 23 deg. C & 0% RH ASTM D 3985	Water Vapour (WV) (g / 100 in^2 / D) at 37.8 deg. C & 90% RH ASTM F 1249
ProtecCore™	< 0.005	< 0.005

Source: Core Laboratories. The laminate is 6.75 mil. thick.

Hunt and Cobb, 1988 determined over a 24 month period, Mylar™ laminate bags had superior moisture retention properties compared to B-60 wax (**Table 11**).

Using no weight loss over time as a quality control measure for Mylar™ bag core preservation may give a false impression all liquids remain in the sample. Unless the majority of air is extracted, liquid and water vapour can move from the rock sample to parts of the packaging and air headspace. **Figure 7** displays the results of an experiment by Wunderlich R.W., 1991[17]. No vacuum was pulled and no attempt made to squeeze air out of the ProtecCore™ bag. The packaging showed little weight loss over the 130 day test while the rock samples actually lost 1 to 6% of their weight. CoreSeal™ wax in comparison performed better but not perfectly at confining liquids to the samples. Wunderlich also made wettability measurements which will be discussed later.

Table 11. Water Loss of RP-40 Preserved Samples Upon Removal from Storage[6]

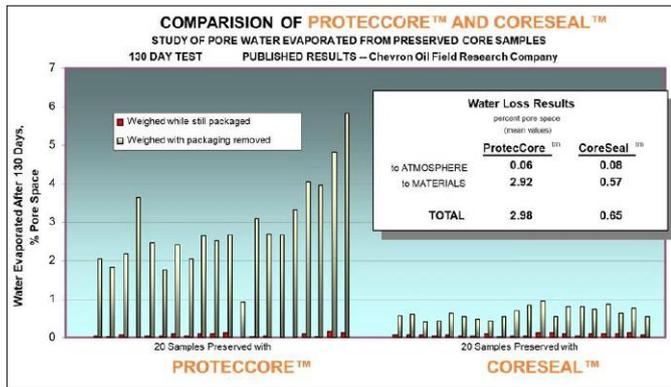| RP-40 Preservation Method	Dean Stark % of Original Content Lost During Storage (+/- 5%)		
	3 Months	12 Months	24 Months
B-60 two dip	20	35	50
B-60 one dip	32	25	80
Laminate Bag	-1	5	2

Hunt and Cobb, 1988

Figure 7. Wunderlich (1991) compared the effectiveness of a laminated (Protec™) bag to a commercial wax (CoreSeal™) for preventing moisture loss from core samples. He found without the air evacuated from the bag, moisture left the rock sample but remained in the laminated bag. The wax proved more effective at preventing moisture loss from the rock samples themselves.

Laminate bags require gentler handling than wax sealed core due to their susceptibility to punctures. Hunt and Cobb (1988) advised to wrap the rock sample before placing it in the bag, as there was danger of puncture from the rock's sharp surfaces[6]. The heat seal should have a width of one inch for confidence the seal is air tight. Gas released from the oil and/or tight rock can expand the bag after sealing. This is not a problem with careful handling.

Modified Atmosphere for Oxidation / Evaporation Prevention

Liquid evaporation and oxidation are enemies of sample wettability maintenance. Waxes, cling films and Al foil wrap enclosures are ineffective for long term wettability maintenance as both oxygen and moisture can pass through or around the materials with time. Heat sealed laminate bags do an excellent job of preventing movement of oxygen and water vapour between the bag interior and the outer atmosphere. However, any oxygen caught in the interior of the bag can alter the sample. Evaporation within the packaging can also occur. To prevent this, the interior gas environment of the bag must be modified. One approach is to add a 1 x 200 cc iron based, self activating oxygen scavenger (**Figure 8**) to the package per foot of core before squeezing the air out of the bag and sealing it. Expect a 20% gas volume reduction if purely air is in the bag. By depleting oxygen levels to very low levels, an atmosphere composed almost entirely of nitrogen is created. Adding a small amount of distilled water (10 cc per foot of whole core) to the package is suggested. This has two purposes: (1) It raises internal humidity levels (High humidity hinders sample water evaporation). (2) Compensates for the iron-based oxygen scavenger drawing moisture from the air for the reaction lowering humidity levels. Desirable is the use of an oxygen scavenger that supplies its own moisture (Ageless® Types ZP, ZPT or RPK® Type K). An enhancement of the technique is to draw a vacuum on the bag followed by a humidified nitrogen flush, followed by another vacuum pull prior to heat sealing the bag[18].

Figure 8. Iron based oxygen scavenger bags.

Heat sealable laminates require less processing time than meltable wax or plastic and are easier to work with. An additional benefit is the rock is not subject to high temperature wax which may disturb the rock fluids.

Sample Immersion

Immersion is a core preservation technique whereby the rock sample is placed in an anaerobic glass or metal container and liquid poured in, submerging the rock. The container may be the core barrel liner itself. The liquid is a deoxygenated synthetic reservoir brine (with added biocide), un-oxidized reservoir crude or nonpolar refined oil. Pressurized (15 to 20 psi) nitrogen or argon fills the chamber's dead space. Argon is preferred to nitrogen to prevent bacterial growth. This is the preferred preservation system for wettability benchmarking. Immersion in a refined oil is the recommended preservation system (**Figure 9**) for shale core targeted for mechanical property tests[19]. Shale is structurally sensitive to any loss of moisture. Irreversible changes occur when rocks with high clay content dry resulting in invalid data[20]. For accurate physical measurements, shales and other high clay content rocks must be preserved at their native water content by immersion in oil[21].

Figure 9. Shale whole core immersed in mineral oil. This is a very effective preservation technique for preventing water loss.

Comparison of Core Preservation Methods

Table 12 compares three core preservation techniques: (1) Mylar[TM] bags, (2) Wrap and Wax, (3) Immersion. Each has its advantages and disadvantages. Mylar[TM] laminates advantage is their extremely low gas transmission across the package interface. Their weakness lies in their vulnerability to punctures and evaporation within the bag itself. To address this, a combination of wrap and wax followed by a nitrogen flushed / vacuumed laminate bag is recommended. The addition of an oxygen scavenger and distilled water to elevate the humidity of any remaining gases in the void space of the bag is a technique yet to be supported by data. Discovered published studies on the effectiveness of core preservation with the exception of Wunderlich's (1991) wettability measurements rely on package condition observations[6] (**Table 13**) and weight loss measurements[11].

Table 12. Comparison of Core Preservation Methods[6,12,13,17]

Criteria	Laminate Bag	Wrap and Wax	Immersion
Evaporation Protection	Excellent	Good	Good
Wettability Alteration Prevention	No clear advantage for any method. For immersion it depends on the liquid used.		
O2 Transmission Resistance	Excellent	Poor - Medium	Excellent
Required Handling of Core	Medium	High	Medium
Ease of Opening and Resealing	Easy, Quick (repeat heat seal)	Time Consuming, New Packaging Required	Replacement of Immersion Fluid
Resistance of Packaging to Long Term Deterioration	High	Low-Medium	High

Hunt and Cobb, 1988. Auman, J.B., 1989. Wunderlich, R.W., 1991. Bajsarowicz, C., 1992.

Table 13. Post Storage Condition of Core Preservation Materials

Field Preserved			
Preservation Method	3 Months	12 Months	24 Months
Wax & Dip (B-60 wax - 2 dips, heavy Al foil, brand name cling film)	Small rips in both the Reynolds 904 PVC film and Al foil.	Many holes in the Reynolds 904 PVC film; Al foil disintegrating.	PVC film very brittle and holed. Al foil badly disintegrating.
Wrap & Dip (B-60 wax - 1 dip, Al foil, generic cling film)	Small holes in both plastic and Al foil.	Many holes in the plastic film; Al foil disintegrating.	Plastic wrap brittle and holed; Al foil disintegrating.
Laminated Bags constructed of Barex, LDPE and Al)	No bag deterioration evident.	No bag deterioration evident.	No bag deterioration evident.

Laboratory Preserved			
Preservation Method	3 Months	12 Months	24 Months
Wax & Dip (B-60 wax - 2 dips, heavy Al foil, brand name cling film)	Pre2004 Saran (PVdC) wrap brittle.	Small holes in Pre2004 Saran (PVdC) wrap.	Many holes in Pre2004 Saran (PVdC) wrap; Some holes in Al foil.
Wrap & Dip (B-60 wax - 1 dip, Al foil, generic cling film)	Many small holes in cling film; Pinholes in Al foil.	Cling film disintegrating; Pinholes in Al foil.	Holes in the Al foil; Cling film disintegrating.
Laminated Bags constructed of Barex, LDPE and Al)	No evidence of bag deterioration.	No evidence of bag deterioration.	No evidence of bag deterioration.

Hunt and Cobb, 1988.

Core Preservation Expiry Dates

The pharmaceutical and food industries provide the consumer with an expiry date (typically 1 month to 5 years from date of packaging[28,29]) for their Al, Al/plastic and plastic encapsulated products beyond which they do not guarantee the freshness and potency of the product. This applies only if the product is stored under suitable conditions, i.e. cool to moderate temperature and moderate humidity. The lack of an expiry date for preserved core has not received attention. Hunt and Cobb (1988) controlled experiments discovered 50 to 80% water loss for a two year preservation period for B-60 Peel Coat[TM] wax, Al wrap, cling film preserved samples but only 2 to 5% for laminate packaging. Auman (1989) investigation showed pore space water saturation reduction of 3 to 16% for wax, Al wrap, cling film preserved core over a five year time span. Over a five year time span, ADNOC Offshore found whole core preserved with the API RP 40 wax and wrap technique, bone dry when opened. The core was stored at U.A.E. climate (high) temperatures. Wunderlich (1991) found wettability change compared to baseline irrespective of the preservation technique in the presence of asphaltic or for a two year storage period. Garcia et al. (2007) found an average of 0.5% pore volume water loss over a 266 day period using the wrap and wax technique and three different commercial waxes. Rousselle at al. (2014) comparing different wax and wrap techniques on core plugs measured water loss over a 31 day period of 1.8 to 8.6% depending on the wax used and the storage temperature. High temperature storage (30 – 40 deg. C) lost more water than lower temperatures (**Figure 10**). The Core Analysis Industry provides no expiry date guidance. Further work needs to be performed in this area to provide specific recommendations.
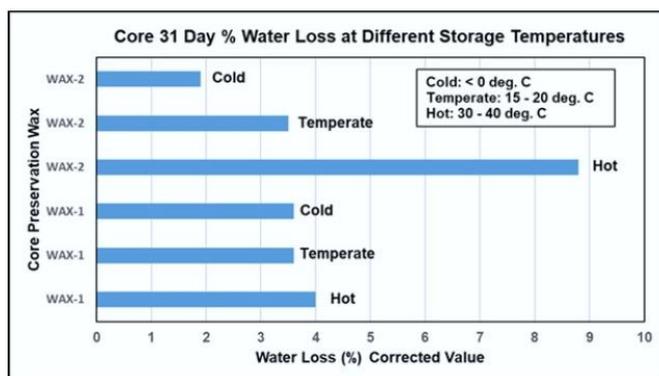
Figure 10. Water loss for RP-40 wax and wrapped preserved core plugs for two different commercial waxes at three different storage temperatures[11].

Elapse Time Prior to Preservation

The time interval between core arrival on surface and preservation can impact results. Significant evaporation loss of gaseous and light hydrocarbons (up to C10) can occur during sample collection within minutes[17, 22]. Water losses for exposed highly permeable (one Darcy) samples reached 15 to 25% of pore volume within two hours (Rousselle et al. 2014). Exposure to air for one day oxidized a core, changing waterflood recoveries compared to a native state core[23]. Richardson et al. (1997)[24] slowed evaporation by placing their Prudhoe Bay sandstone core in six-foot long boxes lined with absorbent pads soaked in diesel while waiting for preservation. Any wellsite examination of cores prior to preservation should be brief to limit oil / core surface oxidation and liquid evaporation. Wunderlich (1991) quotes a case for a paraffinic oil where wettability alteration occurred within 24 hours of the core reaching surface[17]. This demonstrates the importance of the oil's chemistry on whether a preservation technique will succeed or not. He stressed the need to establish a base line reservoir wettability by performing wettability tests immediately on surfacing the core. If the reservoir crude was found to change the rock's wettability, he recommended replacing the native crude with a stable oil as quickly as possible[17].

Storage

Storage conditions, the length of storage time and preservation method considerably affect the outcome of preservation and the experiments which follow. There is a paucity of research on suitable environments for long term storage of rocks and minerals[25]. At the Koichi Core Center, Japan[26], the IODP stores its core at 4 deg. C and 80% humidity with some samples stored well below 0 deg. C. The speed of chemical reactions declines dramatically with decreasing temperature. High humidity slows evaporation loss. Atmospheric humidity and temperature levels are stable to avoid mechanically stressing the rock. Stanley, M. (2004)[27] recommends long term museum storage of rock samples at < 22 deg. C (but not freezing) and a relative humidity (RH) of 45 – 55%.

Conclusions

API RP-40 wrap and wax core preservation suffers from many issues: (1) Variable commercial wax capabilities. (2) Medium to high oxygen permeability. (3) Moderate water vapour permeability. (4) Risk of the core fluids reacting with the cling film and Al packaging. (5) Labour intensive. (6) Slow processing. Studies by Auman (1989), Hunt and Cobb (1988), Wundelich (1991), Garcia et al. (2007) and Rousselle et al. (2014) discovered evaporation can occur over very short time periods for the wrap and wax technique.

Laminates avoid these issues. Their main benefit is extremely low gas permeability. The disadvantages of laminates are: (1) Requires delicate handling. (2) Mylar™ without the addition of a chemical resistant inner layer such as Barex™ risks chemical attack and possible compromise of the package. (3) Fluids and vapours may move out of the core into available void space.

Laminates are superior to wrap and wax for core preservation but can be improved by: (1) Minimizing void space. (2) Controlling the internal atmosphere, humidifying it to minimize evaporation and removing oxygen thereby preventing oxidation.

Core preservation longevity is difficult to judge and is dependent not only on the preservation package but the storage environment. Recommended is weighing of the sample every 6 months to monitor evaporation. Oxidation cannot be monitored presently but is a higher risk for the wrap and wax process than the laminate bag with vacuum technique[18]. If a time limit must be given, 2 to 3 years is offered as preservation limit to the reader.

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