Diverting Agents—History and Application

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Introduction

In 1932 the oil industry started using hydrochloric acid to stimulate oil wells. Immediately the problem arose of diverting the acid treatments into a desired zone, and over the years the diverting methods used have been dictated by the reservoirs being developed. In the period from 1932 to about 1945, the Permian Grayburg-San Andres carbonate reservoirs were primary drilling objectives in the Permian Basin. These reservoirs were from 3,000 to 5,000 ft deep and were generally prolific. Stimulation treatments were usually small in volume (less than 2,000 gal) and the major concern was to avoid acidizing into bottom water. During the period from about 1946 to 1960, Permian reservoirs such as the Clearfork, Tubb, and Spraberry were exploited. These 4,000- to 8,000-ft-deep reservoirs were stimulated with large volumes of acid or fracturing fluids, or both. During the 1960's, deep gas fields (15,000 to 22,000 ft), principally Ellenburger, required new diverting materials to achieve effective stimulation at high reservoir temperatures and pressures.

1936 to 1946

The earliest documentation of a diverting agent was in 1936 when a patent was issued to Halliburton Oil Well Cementing Co. for the use of a soap solution that reacted with calcium chloride to form a precipitate. This was a water-insoluble, oil-soluble calcium soap that acted as a diverting material for the acid.1 One year later Halliburton was issued a patent for a diverting material that utilized locust bean gum to gel calcium chloride and sodium chloride for blanking off a zone and thus diverting acid into untreated intervals.2 Sulfuric acid was used as a diverting agent in connection with a conventional hydrochloric acid treatment. After the sulfuric acid was pumped into the wellbore, the pumps were shut down for a short time and then pumping of the hydrochloric acid was resumed. When in contact with the calcium carbonate, the sulfuric acid formed insoluble calcium sulfate, which was the diverting agent. This system was not widely accepted, owing, it is assumed, to the recognition that it could cause potentially permanent productivity damage.

A major concern in the development of the Grayburg-San Andres carbonate reservoirs was that treatment could extend into the bottom water, particularly since the wells were open-hole completions. Beginning in the late 1930's, various materials were designed to avoid this problem. Dowell developed "Blanket," which was a heavy calcium chloride solution that depended on its viscosity to divert the acid up the hole. Dowell later introduced "Jelly Seal" as the second-generation blocking material. This was a natural gum (locust bean gum) that when mixed with water formed a viscous, gelatinous fluid. When difficulty was encountered in obtaining a plug because of high porosity and permeability, "Jelflake," or cellulose, was mixed with the Jelly Seal to accomplish the shut-off. An internal breaker had to be used to lower the viscosity of Jelly Seal after treatment. For this purpose, a bacteria mixture was prepared by exposing a Jelly Seal mixture to air circulating in a warm room. It was stirred from time to time and liquefaction occurred.

When porous zones or perforations in porous zones are opened for production, the stimulation fluids must be diverted if proper treating is to be assured. It seems that from the time the need for diverting agents was first recognized in the early 1930's, everything has been tried — from soup to nuts.
signaled that the bacteria were ready for use. The original bacteria mixture was then used to inoculate larger quantities. Each station kept a crock of bacteria mixture for use with Jelly Seal. At temperatures below 100°F, 1 gal of bacterial solution was required for each 20 gal of Jelly Seal.7

In the middle 1940's, methods used to divert acids were the "Perimeter" selective acidizing device (Chemical Process) and the "Electric Pilot" (Dowell).4 Each tool located the contact between a conductive fluid (acid) and a nonconductive fluid (oil). The Perimeter and Electric Pilot both used the principle of the "interface locator" and differed mainly in that the power source for the former was located below the surface, whereas the power source for the latter was at the surface. One or more resistors were spaced in an electrode run on a wire line and seated in a tubing nipple set at a preselected depth in the open hole. Acid could be pumped through the tubing and oil through the casing. The interface could be determined by establishing which fluid contacted the electrodes. Where more than one resistor was run, the actual depth of the interface could be controlled quite accurately by varying the pump rates. The reverse of this with the acid in the annulus would permit treating the upper portion of the hole. Disadvantages of this system were that two pump trucks were required and that large volumes of oil were usually needed. In a refinement of this treating method, a blocking material was placed above the electrode, which reduced the loss of oil to the formation and permitted more accurate placement of the acid (Fig. 1).

After the middle 1940's, open-hole formation packers gained widespread use in acidizing. In the Permian Basin, open-hole hook wall packers had usually been used. Many of them were poorly designed and unreliable. One packer used by Shell in the middle 1930's was a "Robinson 80 Hi Pressure Canvas Pack-er." During World War II, packers were unreliable because rubber, a critical material, was diverted to other uses. After the war, rubber element packers were again used as a diverting method. In the late 1940's the Sweet formation packer was developed. It proved to be reliable in diverting stimulation treatments. This packer, which was available with 48- or 90-in. elements, had a side door choke assembly that permitted selective treatment above and below the packer (Fig. 2). Even when fracturing above and below a formation packer with a side door choke, Shell experienced little trouble with stuck packers. This was probably because, as was the practice at that time, they used a large overflush, which displaced the sand from the borehole.

A Lynes straddle packer was first used by Shell in 1945 in the Monahans field. The first attempt to separate a zone for treatment with this packer proved un-

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**Fig. 1**—Diversion in open hole using Perimeter nipple.

**Fig. 2**—Diversion using open-hole formation packer with side door choke assembly.
successful and it was 1949 before further refinements brought it into widespread use. The Lynes packer is a hydraulically operated inflatable packer, excellent for treatment in open holes, particularly in those that have become so enlarged that a regular formation packer cannot expand enough to effect a seal. When the Lynes packers are used as a straddle tool, it is possible to treat three intervals — below, between, and above the packers — without moving the packers. Because it is time consuming to use packers as a diverting tool, it is a more expensive method.

1946 to 1960

In 1947 the use of emulsions to divert acid treatments was begun. Again the locust bean gum was the gelling material, and the resulting emulsion, because of its high viscosity, was used to divert treatment acids.

In the early 1950's, coincident with the introduction of the fracturing process, many different types of diverting agents were introduced. Some new stimulation materials were used for both treating and diverting. In about 1951, when the acid-kerosene emulsion-type fracturing fluids were introduced, Dowell developed "Fixafrac," a blocking agent to be used with them. Fixafrac was a mixture of lime, kerosene, a gelling agent (a fatty acid and a soap), and a graded calcium chloride salt. Oil-external-phase emulsions using Batu gum as an emulsifier were used about this time as diverting agents in fracture and acid treatments. Also in 1951, gelled acids were introduced for acidizing and fracturing. Dowell's "Strata Lift," if used in connection with an acid treatment, would tend to block permeable zones and divert the treatment to less permeable zones. When used as a carrier for sand in less permeable zones, it was a fracturing fluid.6

In 1954 naphthalenes (mothballs) were first used as a blocking material. Crushed mothballs were mixed in a thickened acid. The oil-soluble naphthalene was thought to be the ideal blocking agent because it sublimes above 175°F.5 Naphthalene that sublimes at a higher temperature is now available. Although used earlier in connection with well work, oyster shells were first used in connection with stimulation treatments about this time. Previously they had been used to temporarily block a zone and were removed by acidizing. In about 1954, oyster shells were used with an oil-external-phase emulsion (water-internal-phase) as a blocking agent during stimulation jobs.

With the accelerated search for other blocking or diverting agents, various ones were rapidly introduced. In 1955, crushed limestone and sodium tetraborate were used for diverting. Because the sodium tetraborate is a poison, its use was discontinued and it was replaced by rock salt. Rock salt has had widespread use in the Permian Basin because it is readily available, inexpensive, and easy to handle. In 1956 Gilsonite was used for the first time as an oil-soluble fluid-loss additive and diverting agent.5 Perlite in gelled oil had already been tried as a diverting material. In 1956 guar gum was first examined for use as a diverting agent. Its high viscosity makes it an ideal carrying agent for many of the blocking materials, and it has been widely used in this capacity and as a gelling agent for water-based fracturing fluids.

A major change in diverting agents occurred when ball sealers were developed for better diversion in perforated completions. After World War II and the introduction of jet perforating, the industry began turning to the cased hole as the most efficient means of completion. Since perforation density ranged from 3 holes/ft to as much as 8 holes/ft over long gross intervals (up to 200 ft of 4 holes/ft), the problem of diverting the stimulation fluids was about the same as it had been with the open-hole jobs. Although other methods had been effective in some cases, determining the correct volume of blocking materials was a major problem. In 1956, The Western Co. introduced a rubber ball to be used for sealing off casing perforations and thereby diverting fluids to other perforations.6 Although the first ball sealers were made of solid Hycar rubber and were 7%-in. in diameter, there are now many different types. Ball sealers have been available in sizes from 5%- to 11/4-in. in diameter. Balls containing many different kinds of cores have been used for perforation sealing. Solid nylon balls have been made, as well as aluminum balls, rubber-covered aluminum balls, rubber-covered phenolic balls (stable at high temperatures), and even permeable plastic-consolidated walnut-hull balls (Channelban-Dowell).3 The walnut-shell ball sealers were made so as to permit some bleed-off during a treatment; this would alleviate excessive pressure increases such as those that resulted when perforations were completely shut off by the solid ball sealers.

1960 to 1970

Another technique for diverting stimulation fluids was introduced in 1961 with the concept of limiting the number of perforations. Today, "limited entry" is one of the most efficient methods of diverting. Experience proved that to achieve maximum benefits from a fracture treatment, it is desirable to break down each perforation. This can be achieved with high-rate, large-volume acid treatments, but that approach is expensive.7,8 A better way is to use acid and ball sealers prior to fracturing.

The Frac Baffle, introduced by The Western Co. in 1965, was in effect a new completion technique.8 Used in the Permian Spraberry sandstone (the Upper and Lower Spraberry are approximately 1,000 ft apart), this system was designed for more economical completions in multiple zones. In this method of diverting, one or more baffle rings (baffles of decreasing diameter with increasing depth) were run in the original casing string. These rings (4 in. and 3 in. in size for 51/2-in. casing) are designed to accept a "giant ball sealer" or bomb and effect a complete seal as does a cementing plug. On the completion, the lower zone is perforated and fracture treated through casing. While the flush is being pumped, a bomb is inserted in the casing and the lower zone is sealed off (Fig. 3). With the shut-in pressure maintained, the next zone up is perforated and the next stage of fracturing fluid is pumped. As many as three stages have been applied by this method.

In 1962, a synthetic polymer (Dowell's FLAX-2 and Halliburton's Matriseal) was brought out as a fluid-loss additive and diverting agent. This material
was first designed for use in matrix acidizing jobs in sandstones and has since been used in carbonate reservoirs. The material is inert, but in the presence of acid it swells to 30 to 40 times its original size. The polymer comes in different sizes and shapes, regular and irregular. The particles are pliable, deformable, and degradable.¹,²,³

One interesting method of diverting is the so-called Pine Island fracturing technique widely used in 1964 in the Pine Island field of Louisiana, and in the Luling field of Texas. In this method of diverting a fracture treatment, the lowermost zone is perforated and fractured. The next zone up the hole is then perforated, and before the next stage of fracturing fluid is pumped, the previous perforations are blocked off by plugging back with pea gravel or sand or both. As many as six stages have been performed on a well. One advantage could be that the pressure transmitted through the gravel-sand pack reduces the possibility of communication between the zone being fractured and the previously fractured zone.⁴

Union Oil Co. of California in 1965 introduced "Unibeads" as a blocking material.⁵ This material, which is a special wax-polymer blend of a refinery by-product, is enjoying widespread acceptance. The Unibeads are available with three different 24-hour solubility temperatures (OS-90, soluble at 90°F; OS-130, soluble at 125°F; and OS-160, soluble at 155°F). The material is available in buttons (¼- to ¾-in. in diameter) and in graded particles (from 8 to 100 mesh). It can be used with either water or oil as the carrying medium, and it is oil soluble, water insoluble, deformable, and temperature degradable. Fig. 4 illustrates the pressure behavior for a 5,000-gal acid treatment in a well in Justis field, N. M. The Fusselman zone from 7,153 to 7,204 ft (20 holes) was treated with acid and Unibeads for diversion because of a cement bond failure that had occurred after the initial acid treatment.

Shell's experience with Unibeads in the Mid-Continent Div. Western Region is shown on Fig. 5. The curves are based on results from both acid and fracture treatments. Curve A shows 12 months' afterproduction on 23 jobs and indicates approximately the same decline rate before and after treatment, which suggests that, by properly diverting the stimulation fluids rather than by merely removing skin, additional pay was opened to production. Curve C, reflecting 51 jobs, indicates that production increased 2.1-fold, from 1,400 to about 3,000 BOPD.

In about 1966, "chicken feed" diverting agent was used by Dowell in deep dry-gas wells. This is a ground and graded grain (maize and other feed grain) used as a blocking agent in stage acid treatments. It is a blend of protein, gum, and carbohydrates that will completely degrade in the presence of water, brine, or acid.⁶

Cardinal Chemical Co. introduced in 1967 the treating technique "Temp-Trol," which employed a temperature survey in connection with a stimulation treatment. A base temperature log is run and after one stage of stimulation material is pumped, a second temperature survey is run to determine the interval treated (cooled). Knowing the approximate length of
the interval to be treated, one can estimate more accurately the volume of blocking material needed to divert the next stage. Since both the porosity values and the permeability values for any interval are rarely available, any volumes are estimates at best. In the first treatments, rock salt was used as a diverting material, but since then a variety of other blocking materials have been used.12

In the 1960's, the fluids used for diverting changed very little. The gelled waters, gelled acid, gelled oil, oil-water emulsions and oil-acid emulsions were modified to make them more efficient as diverting fluids and carriers. The variety of bridging materials available was increased during the 1960's and the new materials were basically the result of using more polymer-base materials for blocking.

Paraformaldehyde was introduced as a blocking agent during the late 1960's. This diverting material is used in the deep (18,000 ft and deeper) Ellenburger dry-gas wells now being developed. With the high temperatures — 250° to 350°F — the conventional blocking agents were not adequate for diverting stimulation treatments. Paraformaldehyde is temperature degradable and is soluble in both water and oil. One caution must be noted with paraformaldehyde: when used with a guar gum fluid, the paraformaldehyde will destroy the breaker in the fluid and can prevent it from breaking in the reservoir.

Benzoic acid flakes were successfully used in 1969 and are rapidly becoming one of the most popular diverting agents. Benzoic acid flakes divert by forming a filter cake on the formation. The graded sizes result in a block similar to other solid diverting agents — salt, for example. They have one distinct advantage over other diverting agents in that they are soluble in oil or water. Solubility in aqueous fluids increases as pH and temperature increase. The solubility of the flakes in oil and aqueous fluids is such that these fluids can be safely used as carriers.12 Fig. 6 shows results obtained by Shell in using benzoic acid flakes in fracture and acid treatments. The twofold increase in production is similar to the results obtained with Unibeads. Curve C, reflecting 27 jobs, shows an increase in production from approximately 720 to 1,450 BOPD.

Application

In its completions in the Permian Basin, Shell has used the limited-entry technique since its introduction, or at least a modified limited entry (more holes). Since the number of perforations is limited, all stimulation treatments are diverted, if necessary, by using ball sealers. For economic reasons (excessive hydraulic horsepower is required) ball sealers are normally used on the acid treatment after perforating to insure that all perforations are open. Fracture treatments are usually performed without ball sealers unless there are too many perforations.

The original completion on the deep, dry-gas Ellenburger wells usually requires some method of diversion. Because of the long gross interval — up to 1,000 ft — from 50 to 70 holes are required to open all potentially productive intervals. Shell has employed two approaches in these wells: (1) using ball sealers and (2) pumping a viscous fluid (gelled water) ahead of an acid stage.

One major difficulty encountered with any blocking material is in removing it from the permeable zone after treatment. Any material that depends upon solubility in either water or acid will present a problem in some Wells. If a low-pressure reservoir (Fig. 7) is completely sealed off (which is the case in most of the Permian Basin wells) the ease with which the gel breaks is of paramount importance. The perfect blocking material is one that lasts long enough to divert fluid during a treatment and then becomes ineffective without having to be dissolved by contact with other agents or by internal breakage.

Currently, the diverting agents that most nearly meet these requirements are Unibeads and benzoic acid flakes. The specifications for the OS-90 beads indicate they have a 24-hour solubility at 90°F. However, the melting point of the OS-90 beads is about 138°F. A wax bead with a melting point of 90°F would yield better results for treatments in many shallow wells in the Permian Basin. Benzoic acid flakes have one distinct advantage as a diverting agent: they are soluble in both oil and water, and in low-temperature reservoirs this represents a safety feature not available with most other diverting agents.
A project for research to undertake is the development of a material that stays intact for only the duration of the treatment. Historically, most of the available agents have been designed for long-term breaks (24 hours or longer). Durability, however, is not a requirement for a blocking material.

The value of diverting material necessary for a specific job is difficult to estimate. Since we are able to determine, at best, only the porosity of the zones to be treated and not the permeability, the volume of block must be approximated. The Temp-Trol method of stimulation offers a technique for selective blocking, and when the system is carried to completion it should result in the treatment of all the zones. Although this type of treatment is usually more efficient than normal diverting methods, the additional expense often precludes its use.

Guidelines for Determining Diverting Agent Volumes

In the absence of actual experience in any given field, rules of thumb are used to determine the volume of blocking agent to be used. Following are guidelines for the application of various diverting agents.6, 7, 10, 12, 14

1. Thickened water or oil and emulsions — use 50 to 100 gal per foot of zone to be protected (usually 1,000 gal minimum). The higher range is used if the zone is fractured.
2. Graded Unibeads or graded naphthalene — use 5 lb per foot of zone to be plugged. If in perforations, use 1½ to 2 lb/perforation.
   a. If limited-entry perforations, use 1 lb of material per gallon of carrier.
   b. If multiple perforations, use 2 lb of material per gallon of carrier.
   c. If open hole, use 2 lb of material per gallon of carrier.
   d. In wells with low reservoir temperature, Unibeads should be used in an oil-base carrier to promote dissolving.
3. Benzoic acid flakes — use 10 lb per porous foot of zone to be plugged.
4. Ungraded rock salt — use up to 60 lb per foot to be plugged. If in limited-entry perforations, use 30 lb/perforation.
5. Graded rock salt — use a maximum of 20 lb per foot to be blocked.
6. On a fracturing job, without temperature survey, estimate that 50 ft of zone will be fractured at 20 to 25 bbl/min.
7. Paraformaldehyde — use 5 lb of material per foot to be blocked.
8. Dowell's J-175 ground and graded feed grains — use 5 lb of material per foot to be blocked.
9. Ball sealers (for limited entry):
   a. At a rate of 25 bbl/min and greater, use 10 percent excess.
   b. At rates of 15 to 25 bbl/min, use 30 percent excess.

C. On acid jobs at 4 to 6 bbl/min, use 100 percent excess.

Conclusions

The limited-entry technique or the modified limited-entry technique (using ball sealers) offers the best method of diverting stimulation treatments of new well completions.

In open-hole completions, or in completions with many perforations, Unibeads and benzoic acid flakes have proved to have the most desirable diverting characteristics. Except where temperatures are too low, the plastering characteristic of Unibeads makes them a desirable diverting agent. When reservoir temperatures are too low for Unibeads, the benzoic acid flakes make an efficient blocking material that is soluble in oil or water.

Rock salt, naphthalene or any other solids that depend upon solubility in only one phase (oil or water) to degrade should be used only if no other type of diverting material can be used, and it must be recognized that there is a possibility of damaging the producing zone.

Research is necessary to develop a diverting agent for stimulation treatment that would retain its diverting property for only the duration of the treatment. The diverting agents that depend upon viscosity alone to divert do not appear to offer a positive method of blocking because of the variation and unpredictability of gels and emulsions. A solid that would degrade immediately would be the most desirable diverting agent.

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