

PLAINTIFF'S EXHIBIT

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The Chlorine Institute, Inc.

CHLORINE FACTS

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This booklet has been prepared by the Chlorine Institute, Inc., a non-profit organization, on behalf of its members---producers of chlorine in the United States, Canada and Europe, and manufacturers of chlorine-related equipment. The Chlorine Institute's primary concern is safety---in manufacturing, transportation, distribution and use. Anyone who desires information on the safe handling and use of chlorine is invited to write to the Institute at 342 Madison Avenue, New York, N.Y. 10017.

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Chlorine- Dependable Servant to Man

- More than nine-tenths of the 35 billion gallons of drinking water utilized daily in the United States and Canada depend on chlorine for purity and safety. Had chlorine never been discovered, we might still be boiling much of our drinking water.
- Virtually all of our food supply---material worth some \$50 billion a year---depends on insecticides and herbicides, most of them chlorine-derived, for efficient production. Had these derivatives never been utilized, even so agriculturally rich an area as North America could face severe food shortages and starvation.
- Almost all of the 25 billion yards of textiles produced in the United States and Canada each year depends on chlorine or its derivatives. For man-made fibers, these derivatives provide raw materials; chlorine itself finds a major use in the dyeing and processing of both natural and synthetic fibers.
- Over \$4 billion worth of the paper used each year in North America depends on chlorine or its derivatives for legibility. Without it, our magazines and books might have the readability of something printed on a brown shopping bag.
- Over nine-tenths of the 77 billion gallons of gasoline consumed in the United States each year depend on chlorine for smooth power. Without the anti-knock compounds derived from chlorine, consumers would be forced to pay considerably more for gasoline to match the high-performance engines of today's automobiles.
- Over 120 million tons of steel---about three-fourths of annual U.S. production---depend on chlorine derivatives in being processed into consumer goods.
- The production of such metals as magnesium, titanium, and zirconium is wholly dependent on chlorine. Every bit of aluminum produced in the United States and Canada---some 4 million tons per year---depends on chlorine production.
- Over 14 billion pounds of plastics are produced in the United States and Canada each year. Almost every major class depends on chlorine or its derivatives in some manner---as an ingredient, catalyst or processing aid.

Aerosols. Rocket fuels. Detergents. The list is endless, for chlorine's place in the world we live in can hardly be overemphasized. A recent American Chemical Society computer study* indicates that chlorine is the real "bellwether" among basic chemicals, the one material on which production of other chemicals most depends, the most significant indicator of the nation's prosperity.

But much of chlorine's story remains untold. This booklet has been prepared by the Chlorine Institute to answer these questions: How was it discovered? How did it become important? How is it made and shipped? How does the industry strive to insure its safe handling? How and where is it used? Here are the answers . . .

*Feder, Walter S., *Inorganics Hold Rapid Pace* Chem. & Engrg. News, 45:17,80A (Sept. 4, 1967).

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Chlorine's Early History

The element, chlorine, because of its reactivity, is never found in an uncombined state; rather, it exists in nature in chemical compounds, the most common of which is sodium chloride---ordinary table salt.

Combined in salt, chlorine was a servant to man even before man existed on this earth. Ever since the epoch hundreds of millions of years ago when life first evolved within the saline seas, the chloride and sodium ions in salt have been essential to animal life. As fish evolved into amphibians and then into inhabitants of dry land, their blood, plasma, digestive juices and other body fluids continued to contain a small but absolutely essential amount of salt. Sodium ions control the nerve impulses which guide all activity; chloride ions are essential to the digestion of food.

The evaporation of saline waters to produce crystal salt is said to have first been practiced some 3,700 years ago in China. This process involved the boiling of sea water until the brine became concentrated enough for salt to crystallize out. Making salt through solar evaporation was reported both in China and in ancient Rome, the latter by Pliny the Elder in his "Natural History."

Though in Pliny's time (77 A.D.) no one appreciated the desirability of releasing chlorine from salt, he reported the first step in this direction---the production of hydrogen chloride. In a treatise on the uses of gold in pharmacy, he outlined a process that generated hydrogen chloride gas. When gold is heated with salt, misy (iron or copper sulfate), and schistos (clay), the gold is purified and hydrochloric fumes are emitted as a byproduct. Apparently, there was no interest in examining this byproduct, so the recognition of hydrogen chloride and its water solution, hydrochloric acid, was delayed for many centuries.

Early manuscripts are somewhat confusing, but it appears that the noted Arabian alchemist Rhazes should most likely be credited with the first preparation of hydrochloric acid in about 900 A.D. He gives the necessary directions in his "Instructive Introduction." Soon, sulfuric and nitric acids were also isolated.

Around 1200 A.D., some alchemist tried to dissolve gold in a mixture of concentrated hydrochloric and nitric acids---and succeeded. It is to this unknown alchemical adept, working in a dark and smelly laboratory, that the credit for first producing chlorine must really go, for when gold dissolves in this mixture, chlorine fumes are given off. But he, like the early pharmacist whose production of hydrogen chloride was chronicled by Pliny, apparently paid no attention to the fumes. Thus, recognition of the odor which is characteristic of chlorine again was overlooked.

Finally, in about 1630, chlorine actually was recognized as a gas. A Belgian physician, Jean Baptiste van Helmont in the section "Elementalium Figmentum" in his "Ortus Medicinae," posthumously published in 1648, alluded to many gases---elements, compounds, and mixtures. His gas salium (salt gas) contained chlorine.

The first man to make the pure gas was Carl Wilhelm Scheele (right), a young Swedish apothecary, who isolated chlorine in 1774 as a



byproduct of one of his experiments with a mineral called brownstone. In his laboratory, he ground up the brown-black mineral and poured cold hydrochloric acid over it. When he warmed this mixture, it began to effervesce, giving off a gas. He collected this gas in glass bottles, and observed for the first time chlorine's characteristic odor and yellow-green color. Scheele was also the first man to discover chlorine's bleaching action, for when he placed a variety of materials---yellow, red and blue flowers and green leaves---into these bottles, all became colorless in a few minutes.

Scheele named his green gas "dephlogisticated marine acid" and considered it a chemical compound. It took Humphry Davy, a 30-year-old Englishman, three years to provide definitive proof that the material was a chemical element. He called it chlorine, from "chloros," the Greek word for yellow-green.

Chlorine Finds Its First Use

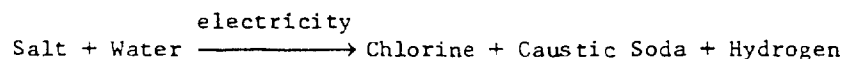
The French were the first to recognize chlorine's commercial utility. Count Claude-Louis Berthollet, who knew of Scheele's bleaching experiments, pioneered its use to bleach textiles. In 1789, someone at a textile mill near Javelle, then a southwestern suburb of Paris, produced chlorine by Scheele's method and bubbled it into a potash solution. The materials reacted to produce potassium hypochlorite---an efficient and easily handled bleach. The name given to this product, Javelle water, is still used by the textile industry as a name for sodium hypochlorite solutions.

Word of the chlorine bleaching process arrived in the newly formed United States before 1800. On December 14, 1798, Cyrus Austin of Burlington, New Jersey, received U.S. Patent No. 214 on a method of generating chlorine and using it to bleach rags for paper. Though his methods seem to be identical to the usual European ones of the day, they apparently were unique enough that Joshua and Thomas Gilpin, who ran a paper mill on Delaware's Brandywine Creek, paid \$500 for a license. Austin, in his patent application, described himself as a paper maker, but it is not known if he produced chlorine commercially in the United States before the Gilpins did. At any rate, the Gilpins were making it as early as July, 1804.

Chlorine Is Produced Electrolytically

Until 1800, the year that Alessandro Volta invented the battery, all chlorine was produced by chemical means. One of the first experiments in which Volta's battery was used was in separating chlorine from salt with electricity. In July, 1800, William Cruickshank, the one-man "chymical" research department of the British Royal Arsenal at Woolwich, reported having electrolyzed ammonium chloride, adding that "common salt was decomposed in a similar manner." He repeated his experiment with salt, and reported that same September that chlorine was evolved. But his work, which pioneered the method used commercially today, was forgotten until after it had been repeated some thirty years later by Michael Faraday.

During the 1830's, Faraday was spelling out the basic rules of electricity, and one facet of this was his study of electrolysis. Among the many thousands of chemical compounds that he decomposed with electricity were sodium chloride (ordinary salt) and potassium chloride. Each of these salts can be electrolyzed in two ways---when heated past its melting point or when dissolved in water to form a salt brine. In 1833, Faraday melted and decomposed these salts into chlorine and metallic sodium, and chlorine and metallic potassium. He decomposed the corresponding salt brines in January, 1834, and set forth the reaction on which most of today's chlorine industry is based:

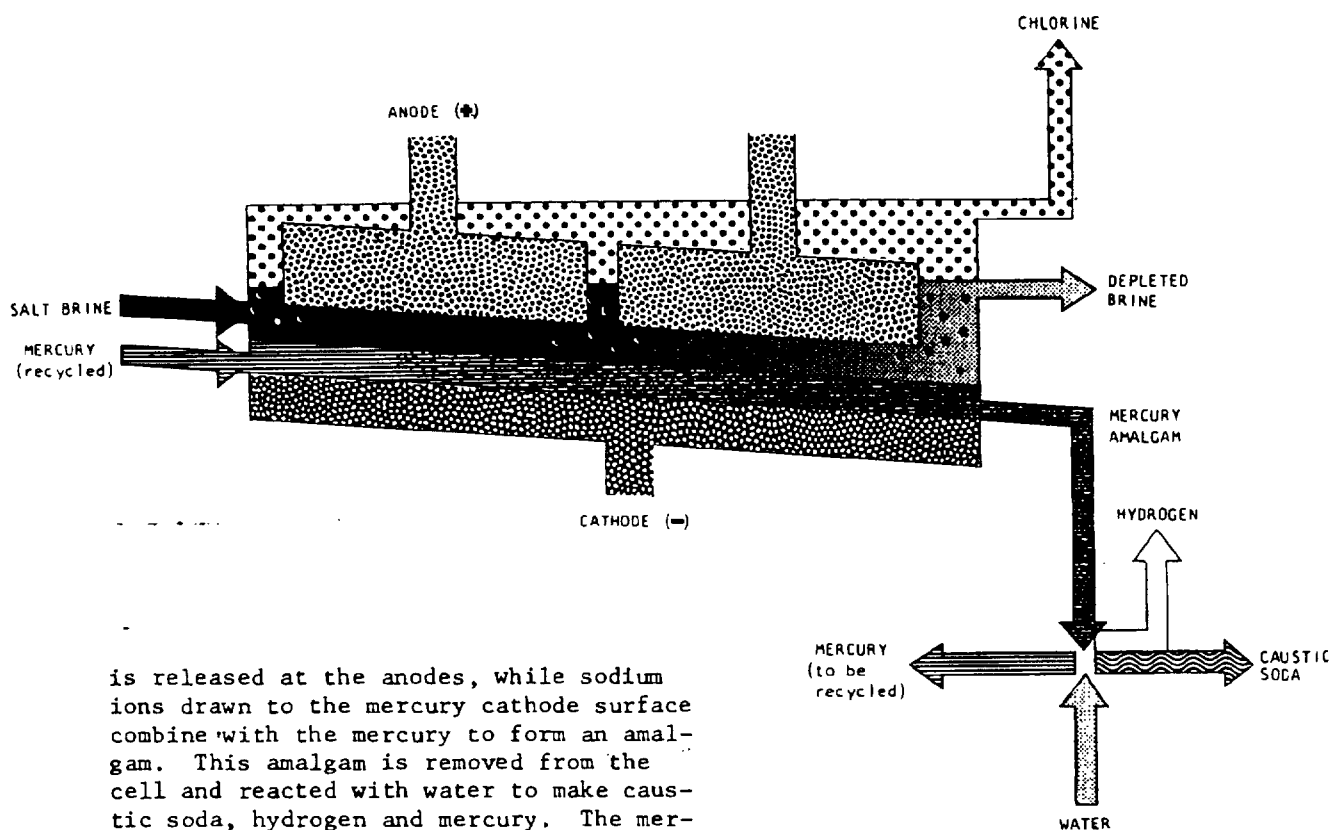


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Chlorine Manufacture Today

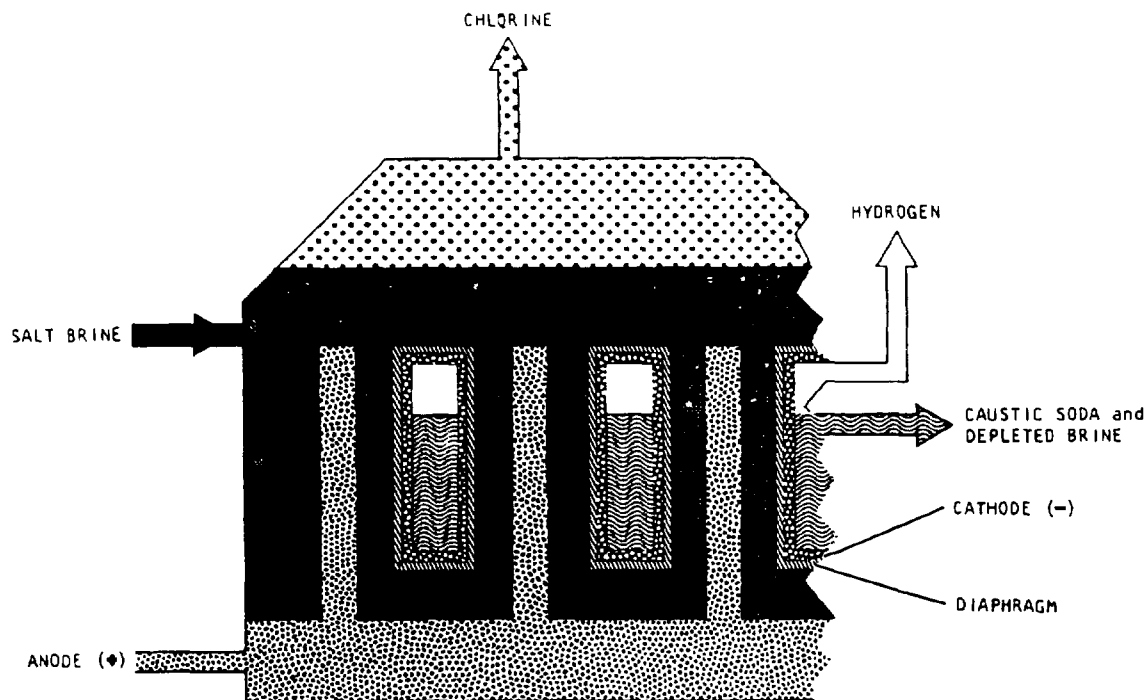
Today, though some chlorine is still made by chemical reactions like the one used by Scheele, most chlorine is produced through electrolysis of salt dissolved in water. Two basic procedures are employed, both designed to overcome the major difficulty in making chlorine: keeping it separate from the caustic soda produced as a coproduct. These procedures, depending on the nature of the separation medium, are commonly known as the mercury and diaphragm processes. The devices in which the electrolysis occurs are called mercury cells and diaphragm cells. Both processes are competitive in today's technology.

In a mercury cell, two liquid layers flow by gravity from one end of the cell to the other. The lower layer is liquid mercury, used as a cathode. Above it is a stream of salt brine, in which are placed graphite anodes. During electrolysis, chlorine



is released at the anodes, while sodium ions drawn to the mercury cathode surface combine with the mercury to form an amalgam. This amalgam is removed from the cell and reacted with water to make caustic soda, hydrogen and mercury. The mercury is then recirculated.

Perhaps the major feature of the mercury process is that it provides a concentrated caustic solution sufficiently free of salt so that it can be used without further purification for many purposes. This process, however, requires somewhat more electric power to make a given amount of product than the diaphragm process. Moreover, mercury is expensive, and high initial and replacement costs are involved.



In a diaphragm cell, the electrolytic reaction products are kept separate by an asbestos diaphragm. When an electric current is applied to a salt solution within the cell, chlorine is generated at the positively-charged anode on one side of the diaphragm. Meanwhile, the negatively-charged cathode on the other side of the barrier attracts dissolved sodium ions, ultimately producing caustic soda and hydrogen gas.

About 70 per cent of the chlorine currently produced in the United States comes from diaphragm cells. In plants under construction in 1968, however, the ratio is about fifty-fifty.

Development of Diaphragm Cells

The diaphragm cell was invented in 1851 by Charles Watt, a chemist from Kennington, England. His cell received little notice until after a practical electric generator had been designed---an event that produced a global flood of new inventions that show the international flavor of the chlorine industry's beginnings. The first American patent on an electrolytic chlorine process went to a Belgian; the first German patent was issued to two Russians; the first practical cell in the United States was the work of a Canadian; the original commercial cell planned for Great Britain was invented by a U. S. citizen and improved by an Austrian; the first major Canadian plant used a Swedish process.

In the United States, the first commercial unit to make bleaching compounds by electrolysis produced a chlorine derivative, sodium hypochlorite. This device, invented by Charles F. Cooper, a British citizen, and Eugene Hermite, an American, was installed in the S. D. Warren paper mill at Cumberland Falls, Maine, in 1888; it employed rotating zinc cylinders for anodes and concave sheets of platinum as cathodes. Mechanical problems were experienced with the rotating cylinders, however, and the device was soon abandoned.

Meanwhile, a number of German experimenters had been at work, and in 1890, Matthes & Weber of Duisburg, the Kunheim Company of Berlin, and Chemische Fabrik Griesheim,

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jointly erected a commercial unit to produce chlorine and caustic potash at Griesheim, using porous concrete for cell diaphragms.

The world's first commercial production of chlorine and caustic soda began in the United States, at Rumford, Maine. The plant was equipped with cells developed by Ernest A. LeSueur, a Canadian, containing an asbestos diaphragm. The Rumford plant, built in 1893 by the newly-formed Electrochemical Company, was so successful that it was expanded fourfold the next year. In 1898, the cells were sold to a predecessor of The Brown Company, which moved them to Berlin, New Hampshire. Some of these original LeSueur cells remained in continuous operation there for the next 72 years.



Development of Mercury Cells



The mercury cathode process was brought to the brink of large-scale commercialization in England by a Brooklyn-born chemist, Hamilton Young Castner. His cells were first operated, however, in Saltville, Virginia, on July 4, 1895, by the American branch of the Mathieson Alkali Works. Because of their high power requirements, the Mathieson company soon moved the cells to Niagara Falls, New York, where a large hydroelectric station had just begun operation.

The new facility was started up on Thanksgiving Day, 1897. Some of the original Castner cells continued in operation there until 1960.

At about the same time Carl Kellner, a Viennese engineer, developed a new mercury cell design which featured a long, slightly inclined trough down which the mercury and salt brine slowly flowed by gravity. Anodes were positioned in the brine all along the trough. At the end of the trough, the mercury entered a decomposing chamber and was then pumped back to run the course once more. It is this design, progressively improved, that is used in most mercury cell installations today.

Both diaphragm cells and mercury cells played a part in early Canadian chlorine production. Some diaphragm cells were operated by the Ontario Peoples' Salt & Soda Company at Kincardine, Ontario, in the 1890's. Apparently these cells were both small and not too successful, for a history of Kincardine published in 1906 makes no reference to them at all. In 1901, a subsidiary of the Lake Superior Corporation brought the first of a bank of 120 mercury cells into operation at Sault-Ste.-Marie, Ontario. While some of the chlorine from this plant, designed by a Swedish inventor, Brodde E. F. Rhodin, went to a paper mill owned by the Lake Superior concern, not enough of the remainder could be sold to make the venture successful. Thus many feel that the real beginning of chlorine production in Canada came on December 31, 1911, when the Canadian Salt Company began operation of its first diaphragm cells at Sandwich, near Windsor, Ontario. This operation was later acquired by Canadian Industries Limited.

Other Chlorine Processes

While the manufacture of chlorine and caustic soda from salt solutions is the dominant commercial method throughout the world, other processes have been used, some on a large scale.

Perhaps the best known of these is the process in which molten salt is electrolyzed to yield chlorine and sodium metal. Such a process was first developed by Charles

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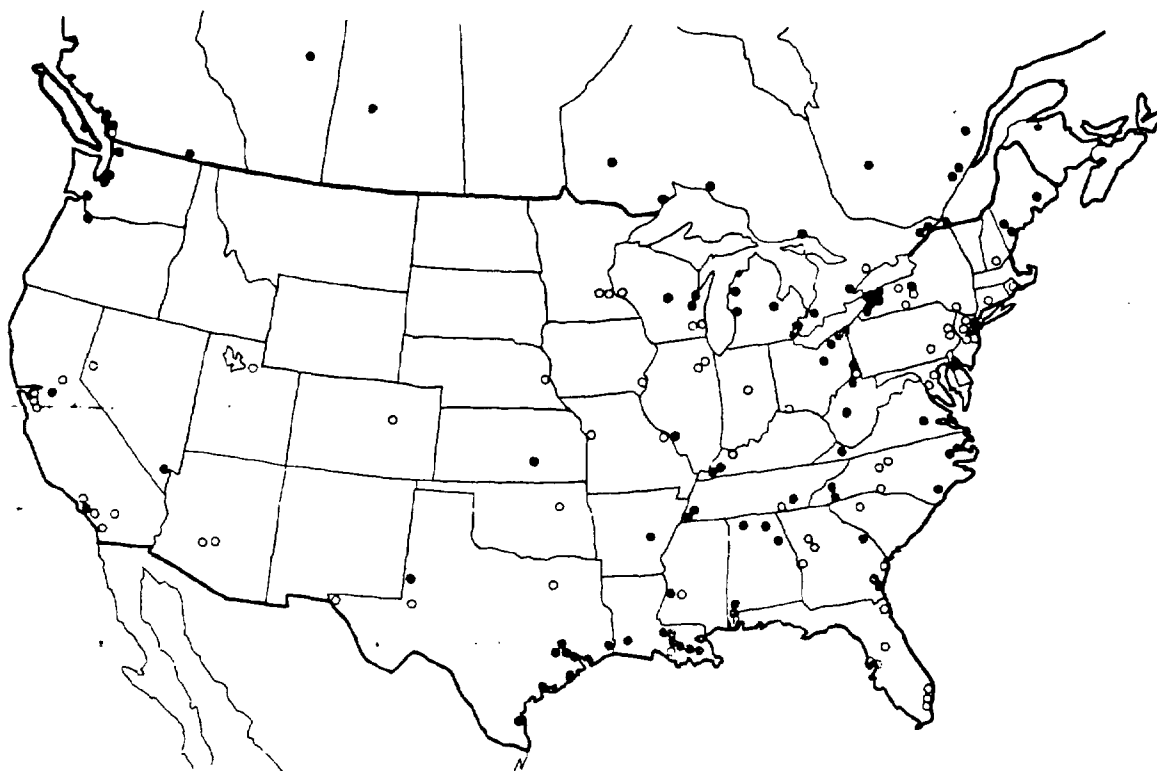
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Acker in 1902 at Niagara Falls, New York. But when his plant was destroyed by fire in 1907, it was never rebuilt. The first really practical cell for making chlorine and sodium metal was patented in 1924 by James Cloyd Downs, who worked for a concern later acquired by E. I. du Pont de Nemours & Company. It is used in five U. S. plants today.

In the early years of the electrolytic chlor-alkali industry, there was a greater demand for caustic soda than chlorine; today, the situation is reversed in both the U.S. and Europe. As a result, there has been a continuing interest in processes for making chlorine that do not involve the simultaneous production of caustic soda. In addition to the five U. S. plants that make chlorine and sodium metal by the Downs process mentioned above, one other non-caustic-producing plant currently operates in the United States. In 1962, the Southwest Potash Corporation (a division of American Metal Climax) began operation of a plant at Vicksburg, Mississippi, to make nitrate fertilizer from potassium chloride. Chlorine is a coproduct.

Yet another process is used commercially in Europe though not in North America. This involves electrolyzing hydrochloric acid to give chlorine and hydrogen.

Other processes are under review. Eventually some of these may add to the North American chlor-alkali industry, which (as of October, 1968) included 96 chlor-alkali producing plants in 24 states and 6 Canadian provinces. Industry output, now valued at almost a billion dollars a year, is growing by over five percent annually.



- Locations of chlorine production plants, October 1968
- Other cities where chlorine repackagers are located

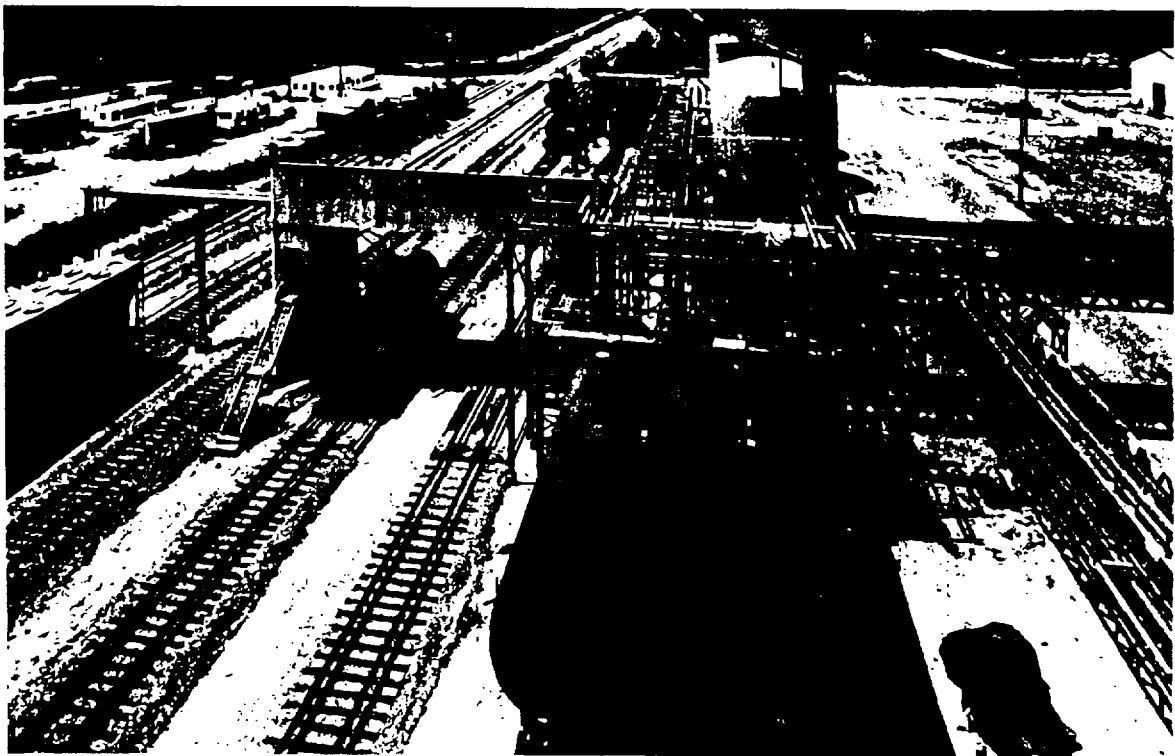
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Chlorine Shipping and Safety

Because electrolytic chlorine manufacture uses a lot of both salt and electricity, most producing plants are located where one or both of these raw materials is abundant, available and cheap. Many chlorine plants are clustered near Niagara Falls, in the Tennessee Valley and along the Gulf Coast. In many instances being located near large consumers is also important.

Shipping Chlorine Safely

The most direct way to transfer chlorine from the manufacturing site to a consumer is by pipeline. This, obviously, is restricted to those situations where it is economically feasible. Many chlorine pipelines, both gas and liquid, exist today. Some are as long as two miles in length, and the number and length of such pipelines are increasing all the time. Approximately one fifth of all chlorine is currently shipped in this manner. Bulk shipment in barges is desirable when both maker and user have access to inland and coastal waterways. This accounts for somewhat less than another fifth of total shipments. Transfer by railroad tank car is the most prevalent approach by far. Shipment in cars with capacities of 16-, 30-, 55-, 85-



Tank car at left is filled with 55 tons of liquid chlorine from foreground storage tanks into which it has been metered from the production unit off picture to the right. At far left are covered hopper cars containing salt, chlorine's raw material.

and 90-tons accounts for about two-thirds of all chlorine shipped in North America. Smaller, but significant amounts are shipped in 100- and 150-pound cylinders, in ton containers, and in highway tank trucks.

Despite the potentially hazardous nature of chlorine if improperly or carelessly handled, the industry has achieved a rather remarkable transportation safety record. For example, in the last five years (1963-67), nearly a quarter million tank cars, containing over 10 million tons of chlorine, were safely shipped in Canada and the United States without a single transportation-related fatality. But this record has been realized only through vigilance. Producers have been cautious in adopting new shipping containers and transfer methods, and continuously review current ones.

Chlorine gas can be readily compressed and liquefied and it is in this form that chlorine in shipping containers exists. Though chlorine was produced in such a form as early as 1806, its transportation was not possible until Rudolf Knietsch of the firm, Badische Anilin- und Soda-Fabrik, discovered that if sufficient moisture is removed from chlorine, it is practical to handle and ship it in iron and steel containers. This event paved the way for chlorine's commercial impact on the chemical industry.

The first large-scale movement of American-made liquid chlorine took place in the autumn of 1909 when the Goldschmidt Detinning Company shipped a 15-ton tank car of the material from Wyandotte, Michigan, to its Carteret, New Jersey, plant for use in processing tin can scrap. This rail freight movement followed by a few weeks the first recorded shipment of American-made liquid chlorine---in six 100-pound cylinders, filled at Niagara Falls by a predecessor of the Hooker Chemical Corporation. In Canada, the first liquid chlorine shipment was made by the Canadian Salt Company in 1921.

Chlorine in Time of War

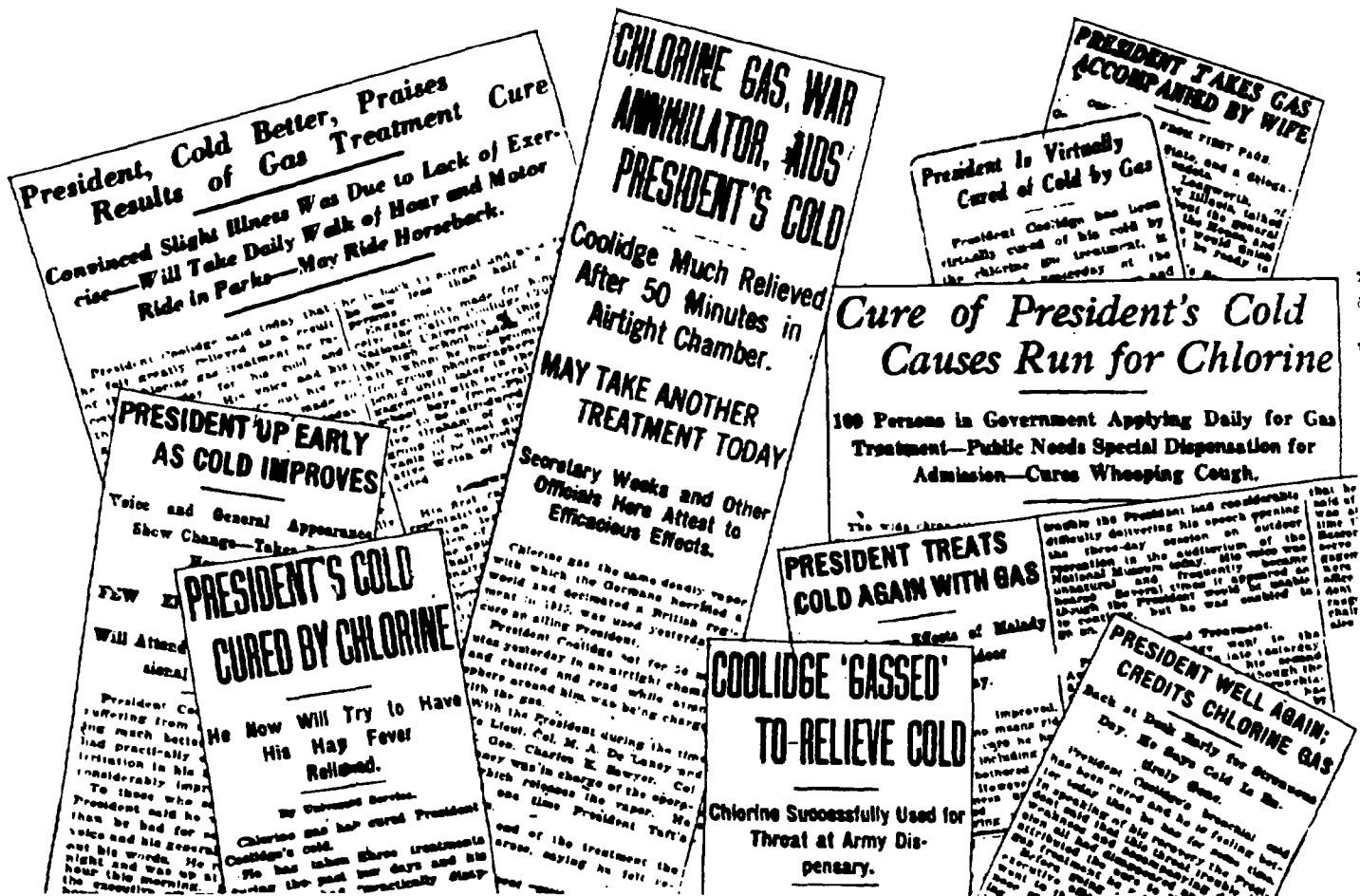
As chlorine became commercially available early in this century, expanded and new industrial uses developed. Regrettably, its easy availability (Germany was then producing it at a rate of 40 tons per day), soon made chlorine into a weapon of war. That it was selected in 1914 was something of a tribute to its utility as an industrial chemical, for though toxic in high concentrations, chlorine would certainly not have already been so widely adopted by industry if it could not be handled safely.

But though chlorine quickly became a weapon, it was almost as quickly discarded as impractical. The containers requisitioned to bring chlorine to the fighting front had been designed for industrial safety and had thick, heavy walls. Their weight made it extremely difficult to maneuver them into and through the muddy trenches.

It took the German army four months after receiving a go-ahead to move enough containers into place for its first surprise attack on April 22, 1915. Many deaths resulted, but chlorine's green color and characteristic odor quickly identified it. Thus, though the Germans followed with a second attack two days later, the Allied troops had already received basic protective devices---simple pads of cotton soaked in ordinary washing soda or soda plus photographic "hypo" to be placed over mouth and nose.

Such simple devices were effective because chlorine is so chemically reactive. In fact, while three times as much gas was used in the second attack, the fatality rate was decreased by 93 per cent. Actual gas masks soon arrived, and gas warfare became little more than a question of inventing and making new chemical gases that the enemy's masks were not yet equipped to handle.

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Within six months, chlorine's short tour as war gas was over. It was made obsolete by other gases ten to fifty times as toxic---gases that were specifically designed for war. After November, 1915, chlorine was not used by itself, but only to mask the presence of these other gases. And it has not been used at all in warfare since July, 1918.

One curious sidelight to the military conflict had its origin only a few years later. A physician at an army chemical plant in Maryland noted that chlorine cell room workers seemed remarkably immune to the common cold. His tests, published by the American Medical Association*, indicated that systematic inhalation of dilute chlorine offered protection against certain bronchial ailments. Certainly the most famous person to receive such treatment was President Calvin Coolidge. In emulation, thousands flocked to special chlorine inhalation rooms. But this application soon fell into disuse. It is not now recommended.

New Challenges for Chlorine Makers

Before 1914, America was heavily dependent on chemical imports from Europe---shipments that thereafter were virtually eliminated by submarine attacks in the Atlantic. But

*Vedder, Edward B. and Sawyer, Harold P., Chlorine as a Therapeutic Agent in Certain Respiratory Diseases. Jour. Am. Med. Assn., 82, 764 (Mar. 8, 1924).

during the military conflict the American chemical industry came to maturity. Chlorine production almost tripled and, since, has steadily increased, bringing new challenges for chlorine manufacturers.

By the early 20's, when chlorine production in North America reached about 150,000 tons per year, it became increasingly evident to chlor-alkali industry leaders that a cooperative effort to develop new markets for their products appeared desirable. In 1924, thirteen merchant chlorine producers formed the Chlorine Institute.

Realizing that no industry could chart a proper course without prompt knowledge of where it stood, a statistics program was immediately launched. Since that time, the Institute has collected data from individual producers, consolidated them and issued monthly statistics on total chlorine capacity, production, and shipment.

Other early institute activities involved research on certain new uses for chlorine, but it soon became apparent that such matters were really the responsibility of individual producers and that the Institute should address itself primarily to the question of safety.

Prior to the Institute's formation, chlorine manufacturers and leading equipment purveyors had their own safety education programs. Their major objective was to educate textile and paper mill workers---the then largest consumers---concerning the greatly different characteristics of chlorine gas from powdered bleaches. Rapid growth of other chlorine applications, especially as a disinfectant, brought about a greater public concern over chlorine use, and a growing awareness by the industry of its responsibilities in promoting safety.

The industry's first major cooperative safety program began in 1926, in the aftermath of a hurricane that devastated Florida. Various suppliers had sent thousands of chlorine cylinders into the state during the crisis for purifying drinking water. It soon became painfully evident that the cylinders' valve fittings often did not match those used at municipal waterworks. Each supplier, it seemed, had his own standards for fittings---which worked well enough in regular times, but not during emergencies. Adapters and new valves were rushed in, and the threat of typhoid, cholera and other epidemics was, in fact, avoided. But the industry resolved "never again," and the Institute thereupon assumed responsibility for setting industry-wide standards for fittings and valves used on chlorine cylinders.

Soon this mission was broadened to include standardization of the fittings on one-ton containers and on rail tank cars. Over a thousand different valve designs were tested and a single one for each use was agreed to. As each selection was cleared by industry committees and other interested parties, it was adopted by every producer. (Remarkably enough, when government officials decided in 1946 to propose equipment standards for all compressed gas containers, they found that the chlorine standards, voluntarily adopted by the industry eighteen years earlier, represented the only such joint effort among producers of all the compressed gases.)

It was at about this same time that the belief developed that the Institute's safety role could be enhanced by investigating and maintaining careful records of chlorine accidents. To the extent that records were available, accident reports for the years 1914-1930 were issued to Institute members in 1931, and annual supplements have continued since. From this activity, modified and expanded over the years, grew the unique industry concept that an accident to one is an accident to all.

Any Institute member, upon call, will send technicians and safety equipment to the scene of an accident, regardless of location, time, the origin of the chlorine shipment, or the nature of the incident---and all without reimbursement. To facilitate

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this service, the Institute maintains up-to-date listings of the locations of chlorine emergency kits. These kits include versatile devices that can, for example, be clamped over leaking or defective valves to seal them. Over 2,000 such kits are available in Canada, the United States and elsewhere. Recently, the Institute has taken over responsibility for the design, production and distribution of such kits to insure their uniform adaptability and thus maximum usefulness.

One early recognition of the Institute's leadership in safety matters came in 1935 when the Institute's secretary was appointed a member of the Association of American Railroads' committee on tank cars*. The secretary has been continuously represented on this committee ever since. Various technological advances in the design, fabrication, loading and shipment of chlorine tank cars---many the work of Institute members ---have been carefully evaluated and tested.

In a similar manner, Chlorine Institute representatives have advised government officials concerned with the shipment of small cylinders and ton containers by truck (beginning in 1935), tank barges (1944) and tank trucks (1960). But such shipments were not started until the industry had assured itself that all such shipments could be appropriately guarded against damage or accident. Throughout, the question of shipping container design has been a prime consideration of the Institute's members---producers and non-producers alike---whose opinions often have been more conservative than those of government officials whom they advise.

Consumer problems relating to the safe handling and unloading of shipping containers also were vigorously pursued. Concern over diverse and often questionable or unsafe container unloading procedures among the ever-growing numbers of chlorine users motivated the industry to propose and disseminate, through the Institute, a variety of safety notes. These eventually evolved into the Chlorine Manual, first published by the Institute in 1947. Since then, the manual has gone into four editions. Better than a quarter million copies have been distributed throughout the world---over a thousand copies each month. This basic education and training tool now is supplemented by some 70 or more other Institute publications relating to various safety aspects of chlorine handling and use, and by personal and group consultation.

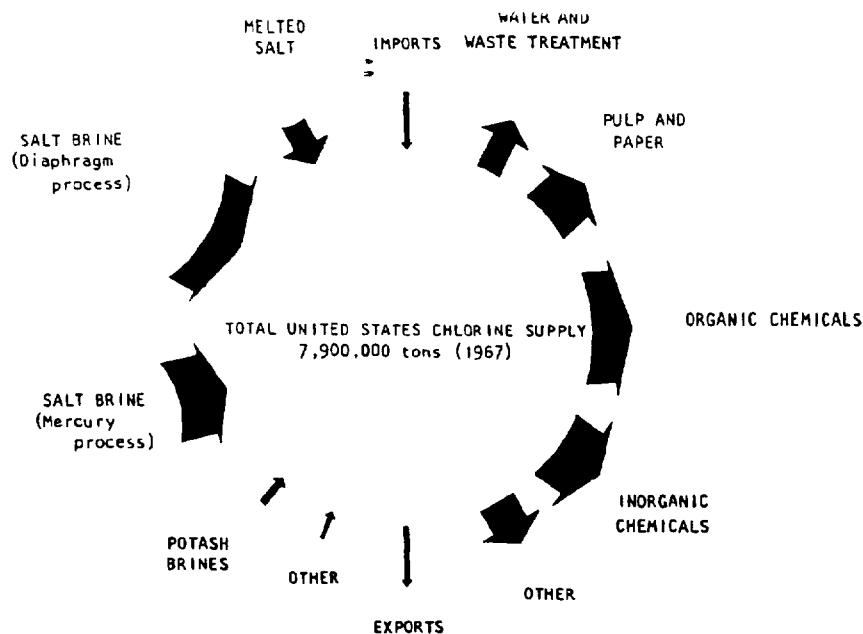
Safety in chlorine manufacture is as vital to the industry as safety in transportation and use. Until the 1950's cooperative industry undertakings in safety matters, through the Institute, had been concerned with the handling of chlorine at and beyond the shipping platforms of chlorine manufacturers. Mindful of government efforts to encourage emergency and disaster preparedness by the chemical industry, and of the desirability of obtaining the free exchange and development of ideas among chlorine producers and repackagers, the first of what now are annual seminars and workshops for chlorine plant managers was held in 1957. These have been of value not only to the participants, but also, where techniques discussed have helped control accidental chlorine emissions, in protecting the general public.

The full story of the industry's efforts to insure the safe manufacture, distribution and use of chlorine and for securing the comfort, health and well being of the public, cannot really be told in these few pages. Vigilance is the industry's watchword, for no action or expense represents too great an effort. Cooperative safety programs undertaken by the chlorine industry over the past five years have cost the Institute's members over a million dollars. Individual company efforts may total as much again. Even so, the industry remains steadfastly dedicated to safety, in manufacture, shipment and use.

*This group had been empowered by the Interstate Commerce Commission to approve applications to build or repair tank cars. The powers and functions of the I.C.C. pertaining to interstate transportation of potentially dangerous commodities in the U. S. were transferred to the new Department of Transportation in 1967.

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A Versatile Spectrum of Uses

Many chemical products, like meteorites in the sky, came out of the void, shone brilliantly, and then plunged once more into darkness. Such new industrial chemicals, once they leave the laboratory, go through a period of spectacular growth, but soon are overtaken by even newer materials. If their production continues to increase at all, it does so in small increments. This is the chemical industry.

But chlorine has proved an exception. Since it came of age as an industrial chemical in the 1920's, its production has continued to outpace total U. S. growth, as measured in Gross National Product:

	<u>1909-14</u>	<u>1914-23</u>	<u>1923-30</u>	<u>1930-40</u>	<u>1940-50</u>	<u>1950-67</u>
GNP increase	13%	119%	7%	10%	186%	175%
Cl ₂ increase	140%	155%	58%	188%	199%	286%

In Canada, production has shown its own steady growth. (Production figures for Canada and the United States are shown in the chart overleaf.)

Of the 8.3 million short tons of chlorine produced in North America in 1967, roughly one fifth is used "as is"---for bleaching paper and in water purification. Chlorine's usefulness as bleach and sanitizing agent depends on its high level of chemical reactivity. When reacted with water, chlorine produces hypochlorite ions ($-OCl$) and hypochlorous acid. It is largely these powerful materials that whiten paper fibers and kill pathogenic bacteria.

Paper bleaching alone consumed over 1.4 million tons of chlorine in 1967. This represents the largest single use for chlorine, and one that shows a healthy growth trend. While the pulp and paper industry as a whole is expanding at a four percent

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per year rate, production of the types of paper that use chlorine in processing is growing at a rate half again as fast.

Chlorine used to purify water and make it safe to drink accounted for some 300,000 tons during 1967---a use that is growing at better than five percent per year. Virtually all of the 35 billion gallons of drinking water processed each day in municipal water plants is chlorinated. And though only about one-third of the waste water treated in industrial and municipal sewage plants is currently chlorinated, the need for ever more intensive usage of all available water supplies will no doubt increase this percentage.

Chlorine Used To Make Other Chemicals

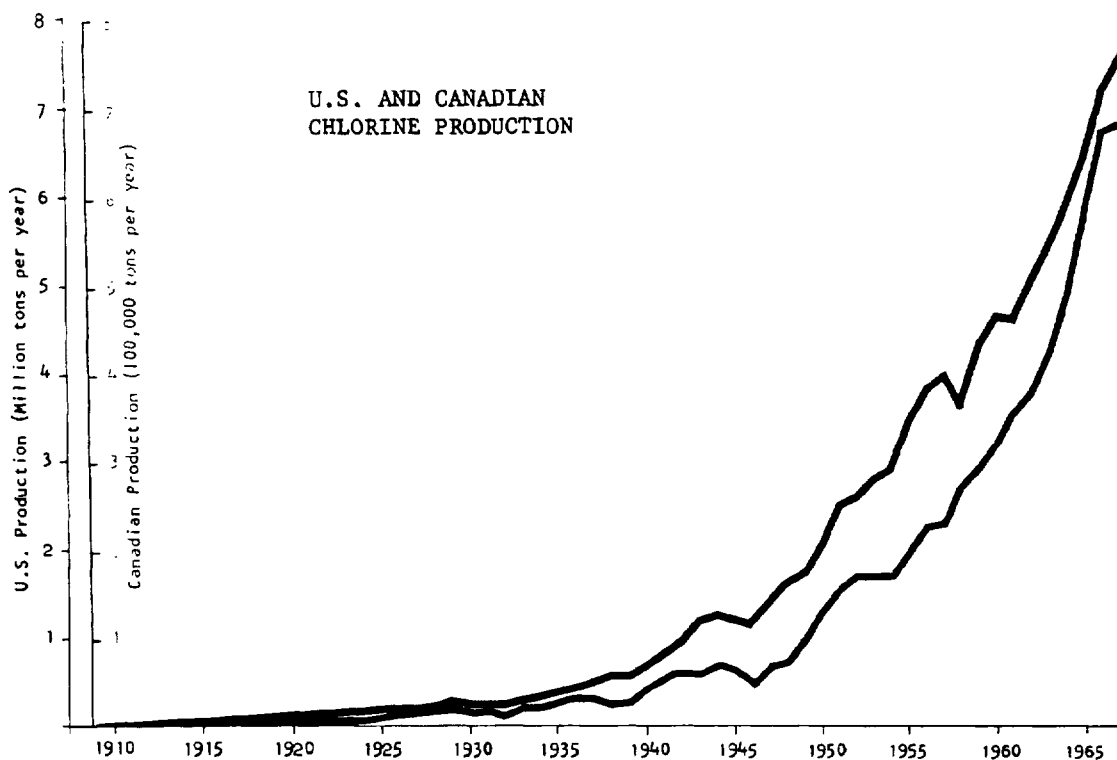
But these uses of chlorine in its elemental form are overshadowed by usage in chemical combination---for this involves four-fifths of total production. In the charts on the following pages, 35 of perhaps a thousand major chemicals dependent on chlorine are classified as to their ultimate uses. In making some materials, hundreds of thousands of tons of chlorine are used each year. On the other hand, there are a few chemicals whose production may amount to no more than a few thousand pounds per year. Such chlorine-derived substances as aluminum triethyl and titanium tetrachloride, in quantities of a pound or so, will cause tons of ethylene gas to polymerize into the hard, waxy plastic known as polyethylene. Such materials, known as catalysts, are no less important to the chemical industry for being needed in these miniscule amounts.

A total of over 6 million tons of chlorine was used to make these chemicals during 1967---an increase of about 50% in just seven years. Much of this increase can be attributed to growth in but two areas---chlorinated hydrocarbons and vinyl plastics. An example of each illustrates the interrelationship of various chlorine derivatives and the over-all pattern of growth.

The simplest organic chlorine derivative, chemically speaking, is methyl chloride, which substitutes one chlorine atom for one of the four hydrogens in methane, a component of natural gas.

First produced in 1835, methyl chloride was for many years a laboratory curiosity. Beginning in the 1920's, however, it found a major use as a refrigerant. Though it is a gas at normal room temperatures, it can easily be compressed into a liquid, and when it is once again allowed to expand, it is an efficient refrigerant. But as it turned out, a newer chlorine derivative called dichlorodifluoromethane (Fluorocarbon 12) was proved even more attractive as a refrigerant. Thus producers set about to find further uses for methyl chloride. Beginning in the late 1930's, this material found major use as a solvent in the manufacture of butyl rubber. Making this synthetic, a material so impervious to air that it was the unanimous choice for use in tire inner tubes, required a solvent that would be a liquid at low temperatures. Methyl chloride filled the bill admirably--until the time in the 1960's when the development of the tubeless tire markedly decreased demand for butyl rubber. So once again, methyl chloride's use pattern shifted--to silicones.

This useful group of chemicals made its debut as "silly putty." But such toy-type use is deceptive, for silicones, because of their high resistance to heat or cold, find many uses in aircraft manufacture and in the U. S. space program. Many of us have utilized these useful compounds in a far more prosaic manner--as a caulking material for the edges of a bathtub. Unlike other caulks, silicones will not shrink with age.



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Gasoline antiknock fluids supply an even newer market for methyl chloride, for this is a key ingredient in making tetramethyl lead, a new competitor to tetraethyl lead. Methyl chloride also finds a horde of miscellaneous uses in plastics, aerosol sprays, hospital disinfectants, food additives, drug processing and metal annealing.

The rapid growth of vinyl plastics provides a further example. Though the basic raw material here, vinyl chloride, was also first discovered in 1835, it was only in 1912 that a Russian chemist realized that this gaseous material could be transformed into a solid plastic. Unable to get his country's Romanov or Communist governments interested in his discovery, the chemist emigrated to the United States. Here, the first plastics made from vinyl chloride were produced in the 1930's, a success story that is even more important today.

The vinyl chloride raw material was made by reacting acetylene gas with hydrogen chloride. This process was efficient only for companies whose other operations produced hydrogen chloride as a by-product. And so, researchers again went to work. They came up with another process. In this, ethylene gas was reacted with chlorine to produce ethylene dichloride. This chemical, when heated under controlled conditions, breaks down into vinyl chloride and hydrogen chloride. As a result, companies with an excess of hydrogen chloride could use the first process; those who needed more hydrogen chloride could use the second. Other companies could use both processes, making half their vinyl chloride needs from ethylene dichloride, and producing the rest by reacting by-product hydrogen chloride with acetylene.

(Text continues after four pages of charts.)

Chlorine's Many Faces -

CHLORINE AND ITS INORGANIC DERIVATIVES		ADHESIVES	AEROSOLS	AIRCRAFT	ANESTHETICS	ANTI-FOAMING AGENTS	AUTOMOTIVE	BACTERICIDES	BLEACHES	CUTTING OILS	DETERGENTS	DISINFECTANTS	DRUGS	DRY-CLEANING	DYE-STEUFFS	ELECTRONICS	EXPLOSIVES	FIRE EXTINGUISHERS	FOOD ADDITIVES	FOOD PROCESSING	FUMIGANTS
Elemental chlorine	$\text{Cl}-\text{Cl}$						✓	✓			✓	✓									✓
Aluminum chloride	$\text{Cl}-\text{Al}-\begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$		✓			✓		✓	✓		✓		✓	✓							
Titanium tetrachloride	$\begin{smallmatrix} \text{Cl} \\ \text{Cl}-\text{Ti}-\text{Cl} \\ \text{Cl} \end{smallmatrix}$		✓		✓									✓	✓			✓			
Zirconium tetrachloride	$\begin{smallmatrix} \text{Cl} \\ \text{Cl}-\text{Zr}-\text{Cl} \\ \text{Cl} \end{smallmatrix}$		✓								✓	✓		✓	✓			✓			
Ferric chloride	$\text{Cl}-\text{Fe}-\begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$																				
Phosphorus trichloride (and related compounds)	$\text{Cl}-\text{P}-\begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$		✓		✓	✓		✓			✓	✓		✓	✓			✓			
Hypochlorite salts	$\text{R}-\text{O}-\text{Cl}$						✓	✓			✓	✓								✓	
Hydrochloric acid	$\text{H}-\text{Cl}$		✓		✓						✓		✓		✓					✓	
Chlorine dioxide	$\text{O}-\text{Cl}=\text{O}$						✓	✓													
Hydrazine	$\begin{smallmatrix} \text{H} & \text{H} \\ & \\ \text{N} & - & \text{N} \\ & \\ \text{H} & \text{H} \end{smallmatrix}$		✓									✓		✓							
ORGANIC DERIVATIVES																					
Methyl Chloride	$\begin{smallmatrix} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{smallmatrix}$	✓	✓	✓		✓	✓	✓			✓	✓		✓					✓	✓	✓
Methylene chloride	$\begin{smallmatrix} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{smallmatrix}$		✓	✓		✓					✓			✓		✓					
Chloroform	$\begin{smallmatrix} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{smallmatrix}$		✓		✓							✓		✓							✓
Carbon tetrachloride	$\begin{smallmatrix} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{smallmatrix}$		✓	✓		✓	✓				✓	✓					✓				✓
Fluorocarbon 12 (and similar compounds)	$\begin{smallmatrix} \text{F} \\ \\ \text{F}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{smallmatrix}$		✓	✓	✓	✓					✓						✓		✓		
Phosgene	$\text{O}=\text{C}-\begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$	✓		✓		✓								✓							
Ethyl chloride	$\begin{smallmatrix} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ & \\ \text{H} & \text{H} \end{smallmatrix}$			✓		✓					✓			✓							

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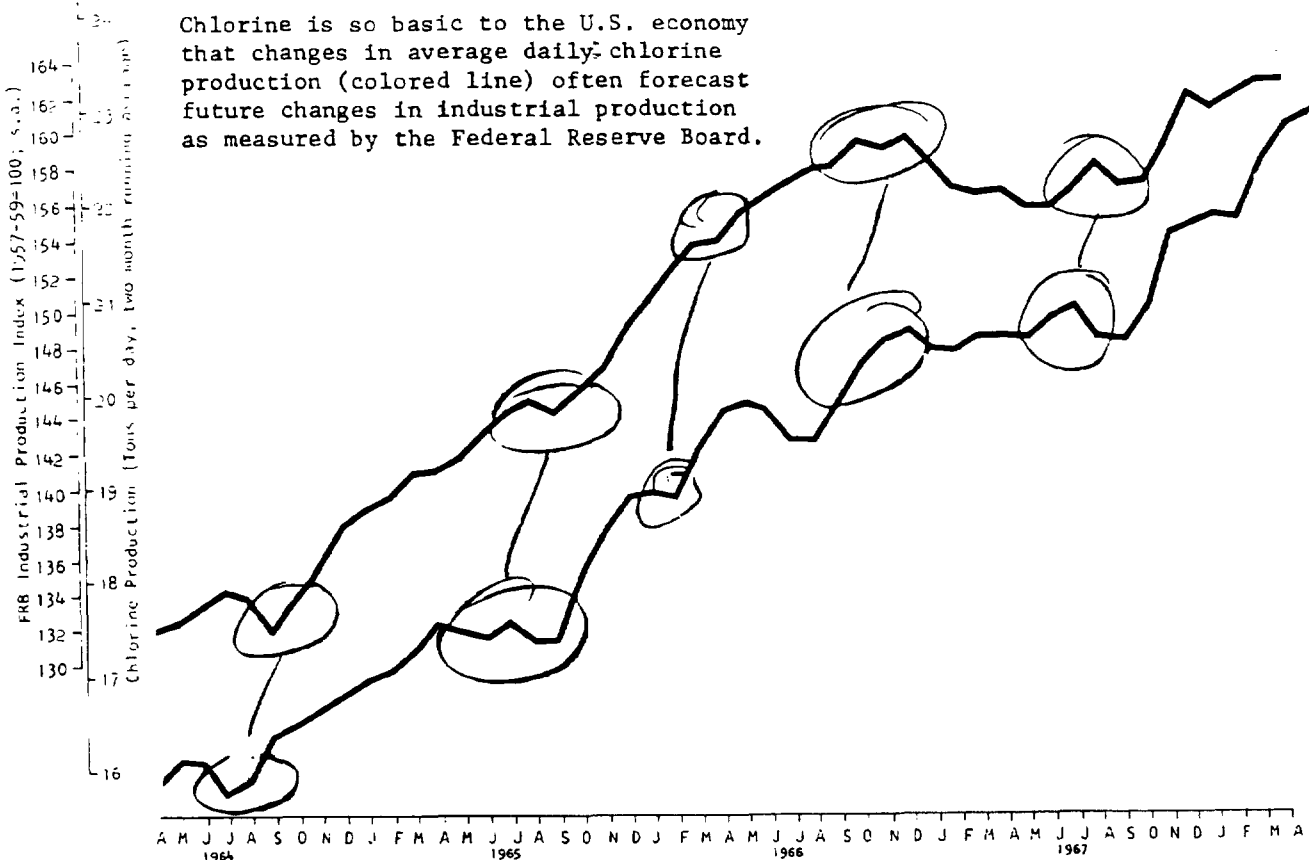
		ADHESIVES	AEROSOLS	AIRCRAFT	ANESTHETICS	ANTIFOAMING AGENTS	AUTOMOTIVE	BACTERICIDES	BLEACHES	CUTTING OILS	DETERGENTS	DISINFECTANTS	DRUGS	DRYCLEANING	DYESTUFFS	ELECTRONICS	EXPLOSIVES	FIRE RETARDANTS	FIRE EXTINGUISHERS	FOOD ADDITIVES	FOOD PROCESSING	FUMIGANTS
Ethylene dichloride	<chem>ClC(Cl)CCl</chem>	✓	✓		✓									✓							✓	
Trichlorethane	<chem>CCl(C)CCl</chem>		✓	✓	✓								✓	✓						✓		
Vinyl chloride	<chem>CC=C(Cl)</chem>	✓	✓		✓									✓								
Trichlorethylene	<chem>CCl(CCl)CCl</chem>		✓		✓								✓	✓						✓		
Perchlorethylene	<chem>CCl(CCl)CCl</chem>		✓		✓								✓	✓						✓		
Ethylene chlorhydrin	<chem>OCC(Cl)CCl</chem>	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓				✓	✓	✓	
Chloral	<chem>CCl(Cl)CCl</chem>		✓	✓								✓										
Monochloroacetic acid	<chem>CCl(Cl)CCl</chem>		✓									✓							✓	✓		
Allyl chloride	<chem>CC=C(Cl)CCl</chem>	✓	✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓				✓	✓		
Epichlorhydrin	<chem>OCC(Cl)CCl</chem>	✓	✓		✓			✓				✓	✓	✓								
Glycerine	<chem>OCC(O)CCl</chem>	✓			✓							✓		✓	✓				✓	✓		
Propylene oxide	<chem>CC1OC1CCl</chem>		✓		✓	✓		✓	✓	✓		✓		✓					✓	✓		
Hexamethylenediamine	<chem>NCCCCCNC</chem>		✓		✓									✓								
Chlorinated paraffins	<chem>CCCCCCCCCl</chem>		✓		✓			✓	✓									✓				
Chlorinated benzenes	<chem>c1ccccc1Cl</chem>	✓	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓							✓	
Chlorinated phenols	<chem>Oc1ccccc1Cl</chem>				✓																	
Trichlorocyanurate	<chem>ClC1(Cl)C(Cl)N1</chem>				✓	✓		✓	✓	✓	✓											
Hexachlorocyclopentadiene	<chem>ClC1(Cl)C(Cl)C(Cl)C1</chem>																✓					

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FUNGICIDES	GASOLINE	GERMICIDES	HERBICIDES	HOUSEHOLD CHEMICALS	HYDRAULIC FLUIDS	INSECTICIDES	METAL PROCESSING	MISSILES	MOTHPROOFING	NUCLEAR REACTORS	OIL PAINTS	PULP AND PAPER	PERFUMES	PIGMENTS	PLASTICS	PLASTIC FILMS	POLYFOAMS	PROTECTIVE COATING	REFRIGERATION	ROCKET FUELS	SANITIZING	SEWAGE TREATMENT	SILICONES	SOFT DRINKS	SOLVENTS	SUPERPLASTICS	SYNTHETIC FIBERS	TEXTILES	TITANIUM	TOBACCO	WATER PROCESSING	WATER REPELLENTS	WOOD PRESERVATIVES	ZIRCONIUM
✓		✓							✓					✓	✓	✓																		
					✓	✓		✓	✓														✓											
		✓								✓	✓				✓	✓	✓								✓	✓	✓					✓		
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		✓		✓				✓																										
		✓	✓	✓	✓		✓				✓												✓				✓				✓			
		✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						✓	✓	✓					✓				
		✓						✓	✓						✓	✓	✓						✓	✓			✓				✓			
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		✓			✓								✓											✓	✓			✓						
		✓		✓	✓	✓	✓	✓					✓	✓	✓	✓		✓	✓												✓			
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And what can a plastics technologist do with vinyl chloride? Practically anything. Today, well over two billion pounds of polyvinyl chloride plastics are produced in the United States and Canada each year, making it one of the three major types of plastics. Almost one quarter of this---500 million pounds---is accounted for by upholstery, wall coverings and other types of film and sheeting. Vinyl floor tiles take 300 million pounds more, while the insulation around wire cable and rigid vinyl pipe each account for 200 million pounds. The use of vinyl materials in paper and textile coatings, and as phonograph records rank close behind. Vinyl chloride, when mixed with related raw materials like vinyl acetate, make a further wide range of "copolymer" plastics.

All these uses for chlorine derivatives have created a continuing momentum of growth ---at a rate that has confounded some market research specialists. In 1953, one chemical weekly estimated that production should increase from 2.8 million tons per year to 3.24 million tons by 1960. The actual 1960 production was 4.64 million tons, 45% over the estimate. In 1961, another chemical news magazine forecast production of 5.7 million tons by 1965. This figure was exceeded by almost a million tons. A detailed 1964 study by one reporter predicted 7 million tons by 1970, only to see that target reached in 1967.

What will prompt chlorine's next spurt in growth? It may be a new rocket fuel component. Or perhaps a major new use for a vinyl plastic. Some researchers feel that chlorine will be used in combination with lithium metal to energize a fuel cell powerful enough to run the first really practical electric automobile.

Truly, if there is one thing that can be expected from chlorine, it is that it will continue to exceed expectations.

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For Further Reading

CHLORINE'S EARLY HISTORY

"Exceeding All Expectations. A Short History of Chlorine," New York: The Chlorine Institute, 1968. This reference is an anecdotal history of chlorine from which the historical material in this pamphlet has been excerpted.

Partington, J. R., "A History of Chemistry," London: Macmillan, 1961-4. Though volumes 2-4 of Partington's history are organized chronologically by personalities, an excellent index makes this a very convenient source on chlorine's history after 1500. Partington's volume 1, still to be published, will undoubtedly do the same for earlier years.

Forbes, R. J., "A Short History of the Art of Distillation..." Leiden: E. J. Brill, 1948. This is a valuable reference on the early preparation of mineral acids.

Kopp, Hermann, "Geschichte der Chemie," Braunschweig: Friedrich Vieweg, 1843-7. Though somewhat dated, this is the basic German text. Discussion of chlorine's early history begins on p. 349 in volume 3.

Urdang, Georg, "Carl Wilhelm Scheele: a Pictorial Biography," Madison, Wis.: American Institute for the History of Pharmacy, 1956. This reference sets Scheele's work with chlorine within the context of his career.

Additional Chlorine Source Documents

Scheele, Carl Wilhelm, "Om Brunsten eller Magnesia, och dess Egenskaper," Kongliga Vetenskaps Akademiens Handlingar, 35, 89 (April-June, 1774). This is Scheele's original report. An English translation appears in "The Early History of Chlorine," Alembic Club reprints, No. 13. Edinburgh: W. F. Clay, 1897. The translation is marred by a continuing reference to "manganese" when manganese dioxide is clearly intended.

Davy, Humphry, "The Elementary Nature of Chlorine," Alembic Club reprints, No. 9, Edinburgh, 1929. This reference provides Davy's proof that chlorine is an element.

Cruikshank, William, "Some Experiments and Observations on Galvanic Electricity," Journal of Natural Philosophy, Chemistry, and the Arts, 4 (first series), 187 (July, 1800); "Additional Remarks on Galvanic Electricity," Ibid. 4, 254 (Sept., 1800). These references include the first reports of the electrolysis of salt to produce chlorine. The chemist-author should not be confused with a second William Cruikshank (1745-1800), physician and anatomist.

Faraday, Michael, "Experimental Researches in Electricity," Vol. 1. London: R. & J. E. Taylor, 1839. This records the electrolysis of brines and fused salts by the developer of electrochemistry.

Faraday, Michael, "Liquefaction of Gases," Alembic Club reprints, No. 12, Edinburgh, 1904. This also contains Thomas Northmore's report of his liquefaction method, 17 years previous to Faraday.

CHLORINE MANUFACTURE TODAY

Sconce, James S., editor, "Chlorine: Its Manufacture, Properties and Uses," New York: Reinhold, 1962. This monograph

is the most extensive source of information on chlorine today. In 29 chapters, each with a bibliography, a wide range of information is presented. As in any book with many contributors, there is some variance among chapters, but except for early history, this is the basic technical reference.

Hardie, D. W. F., "Electrolytic Manufacture of Chemicals from Salt," London: Oxford University Press, 1959, reprinted in 1965 by The Chlorine Institute. This provides a short, authoritative review of modern chlorine production practices.

"Chlorine Summary Statistics: United States and Canada," Chlorine Institute pamphlet No. 11. Reissued annually.

"Chlor-Alkali Producers and Chlorine Repackagers in North America," Chlorine Institute pamphlet No. 10. Reissued annually.

"Chlor-Alkali Producers Outside North America," Chlorine Institute pamphlet No. 16. Supplemented and revised periodically.

Audio-visual Aids

"Chlorine -- a Representative Halogen," a 15 minute 16mm sound/color movie produced as a highschool chemistry instruction aid for the Manufacturing Chemists' Assn. Available on loan from MCA, 1825 Connecticut Ave., N.W., Washington, D.C. 20009, or Sutherland Educational Films, 201 N. Occidental Blvd., Los Angeles, Calif. 90026.

"The Electrolysis of Brine," an 8-1/2 minute 16mm sound/color movie that shows classroom demonstrations and commercial production techniques, produced for PPG Industries. Available on loan from Association Films, 347 Madison Ave., New York, N. Y. 10017.

"Commercial Production of Chlorine," a 9-1/2 minute 16mm sound/color movie produced for PPG Industries. Available on loan from Association Films, 347 Madison Ave., New York, N. Y. 10017.

CHLORINE SHIPPING AND SAFETY PRACTICES

"List of Available Pamphlets, Drawings and Miscellaneous Publications," New York: The Chlorine Institute. Reissued semi-annually.

"Chlorine Manual," Chlorine Institute pamphlet No. 1. This represents a compendium of experience available to the Institute on the safe handling and use of chlorine.

"Types and Location of Chlorine Emergency Kits in North America," Chlorine Institute pamphlet No. 35. Supplemented and revised periodically.

Miscellaneous chlorine fact booklets, available from many chlorine manufacturers.

Audio-Visual Aids

"Chlorine Safe Handling," a 30-minute 16mm sound/color movie produced for PPG Industries. Available from PPG Industries, Inc., Chemical Div., One Gateway Center, Pittsburgh, Pa 15222.

Other films and film strips are listed in Chlorine Institute pamphlet No. 58.

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