DISCUSSION OF THE

Requisite Qualities of Lithographic Limestone,

WITH

REPORT ON TESTS OF THE

Lithographic Stone of Mitchell County, Iowa.

By A B. Hoen.*

In order that a good understanding may be had of the subject of this article, it will be necessary to give a description of the process of lithography and the principles on which it depends for its successful working. These principles are very simple in nature.

In the dawn of the preceding century Alois Senefelder, a young Bavarian playwright and composer, to save expense, sought some cheap means of producing editions of his works. He first tried copper engraving, but as the plates were quite expensive and the use of the same plate for subsequent engraving involved the tedious grinding out of the existing engraving and the resurfacing of the metal, he found his means and time inadequate. He had been using slabs of Solenhofen limestone as mortars on which to grind and mix his copper plate inks. In the absence of a suitable piece of paper, he one day made a memorandum on a clean

* As noted in the body of the report on Mitchell county, samples of the lithographic stone from the quarries near Osage were submitted for trial to the lithographing house of A. B. Hoen & Company, Baltimore. Mr. A. B. Hoen generously undertook the task of subjecting the stones to all possible practical tests. For this service, and for the accompaning discussion of the qualities which a serviceable lithographic stone must possess, the Survey gratefully acknowledges its obligations. Plate VIII, printed on a sample of the stone from Mitchell county, illustrates the quality of the work which may be done with lithographic stone from Iowa. S. C.

slab of this stone, using as ink a fluid made of wax, soap, lamp-black and water. He had previously used this same preparation to cover up mistakes in his copper engraving before etching. It occurred to him, on looking at the dried writing on the stone, that the same ink might offer a good resistance to acid and that, perhaps, the letters might be brought into relief by etching and then used, as wood blocks were, for surface printing. Etching with nitric acid proved the correctness of his reasoning and he was able to ink letters, now standing in relief, with an ink ball or tampon and to obtain prints from the inked surfaces by applying paper under pressure. This, happening in 1798-99, was the beginning of lithography. The new art was soon in great demand, its principles were taught to some qualified disciples and its practice was begun in many places. Senefelder in 1818 produced an extensive treatise on his art, which easily supplanted all previous writings on the subject. It will be noticed, however, that the plates resulting from the process as described, differed in no essential feature from those of the typographer of that day or of the present. The design or lettering to be printed was made to stand in relief, so that only the raised surfaces would take ink from the inking roller and, in turn, communicate the impress to the printing paper. From the beginning, as made by Senefelder, came several unexpected results. It was found, if ink containing soap or grease were used to make the drawing on stone, that it was not necessary to etch the design into high relief, but that the greased parts would take ink and the ungreased parts would remain clean, provided the stone was kept damp during the operation of inking. This was the greatest advance made in the art since its discovery and indeed is the basis of modern lithography.

The Solenhofen stone is a compact, amorphous limestone. The cleanly polished surface will absorb water, not as rapidly as chalk, but in the same manner. It is porous. Therefore such a surface, the mass having an affinity for water, can be kept evenly moist by wiping or rolling with a wet sponge or cloth. As long as the surface of the stone is moist, grease and greasy or oily inks will not attach themselves to it. They are prevented, by the film of water, from actual contact. Conversely, if the clean, dry surface be covered with grease or varnish, the pores of the stone will be filled and the stone will be no longer capable of absorbing water through its greased surface. Even if water be poured on such a greased stone, it would not moisten it with an even film, and an inking roller would secure contact with the surface and discharge the ink.

Making use of the repugnancy of grease and water for each other and of the power of the stone to absorb, we should expect and find that a design traced or drawn with greasy ink or greasy crayon on a clean stone, would fill in the pores of the stone in those parts covered by the design, and that the same parts would locally repel water and attract grease or greasy ink.

The application and improvements of mechanical devices to the carrying out of this fundamental principle mark the stages in the progress of lithography from the time of its discovery to the present.

It might be asked, is the compact, amorphous limestone the only material that will respond to this dual treatment with water and grease? By no means. Grained glass will carry a grease design for a short time, but if the grease be washed out of the grain with some solvent, the design will be found to have disappeared and cannot be developed by further application of ink and water. A design or image formed on lithographic stone may be washed out so that none of the ink remains on the surface, but may be brought back by treatment with water and ink together—the ink taking to the previously greased parts and the water keeping the previously clean parts from taking ink. These two sets of phenomena lead to an explanation of the principles underlying the lithographic process. The image on the glass could be removed completely by solvents of grease, but the image in the stone was more firmly seated and could not be removed by these media. Evidently the stone was affected by the grease in a way different from the glass. My experiments have shown that if fixed vegetable or animal oils be brought in contact with clean dry limestone, they will penetrate it, mechanically fill its pores. and thus make a printable image. This image, however, may be removed if solvents, such as benzene, be copiously applied shortly after the oil and stone have been brought together. Prolonged action of the oil on the stone leads to a chemical as well as physical union, i. e., the fatty matter not only fills in the pores of the stone, but also replaces the carbon dioxide (CO_2) of the stone and forms a calcium salt of the fatty acid. This calcium salt is insoluble in both water and grease solvents and the image thus formed is therefore permanent. An image of like permanency may be formed by impregnating the stone with some light sensitive material which will attract grease and repel water—asphaltum for instance. If an image be formed in the stone with thin asphalt and be rendered insoluble in turpentine by exposure to sunlight this image will behave, for all practical purposes, in the same way as the fatty-acid lime salt. When such an image is inked in the usual way the grease of the ink ultimately combines with the lime and the resulting image is the same as previously formed by direct application of grease or oil to the clean stone.

As stated above, the formation of the fatty-acid lime salt, say calcium oleate, may be prevented by solvents if the latter be quickly applied. The combination takes place much more rapidly if the fatty acid itself be used in place of its glycerine salt.

The most efficacious means of all, however, for producing this combination is by the double decomposition of an alkali salt of the fatty acid (soap), and the stone by means of one of the mineral acids. In other words, if the image be drawn or laid down on the stone with crayon containing soap and then etched with a solution of hydrochloric acid, the soda of the soap will be taken up by the hydrochloric acid (HCl), the fatty acid will be set free and will combine immediately with the lime of the stone to form a lime soap. This forms the latent image in lithography and when the stone is washed clean with water and turpentine it may be faintly seen by reason of the difference in color of the calcium oleate from the surrouning carbonate. The latter too has a matte or etched appearance on account of the action of the hydrochloric acid (HCl).

While the acid fixes the greasy image in the stone, it has a further role to play in keeping the ungreased parts clean. It was found in practice that acid (HCl or HNO_3) and the calcium salts resulting from its action on the stone were far better than plain water in keeping the open parts—the ungreased parts—clean. They filled the pores of the stone and, even if the stone dried, prevented combination with grease fortuitously coming in contact with it. A still further improvement in this direction was made by the addition of gum arabic or similar colloid substance to the etching fluid. The gum penetrates the surface of the stone and forms a film on it and at once prevents the taking on or spreading of the greasy ink and at the same time is ever ready to take up moisture. So firm a hold has the gum on the stone that if a clean stone be gummed and the gum allowed to dry, oil or greasy ink may be smeared over this gummed surface without affecting the stone, which will come out perfectly clean on application of water.

With these principles in mind we may now look into the two major subdivisions of the lithographic art, consideration being had for the characteristics of the stone which facilitate or impede its practice.

The first process is to apply the grease locally by means of fine pens or brushes to the surface of a clean stone. If the stone had been previously grained with fine sand the local application of the grease may be made with lithographic crayons, which are composed of lamp black and hard soap.

The gradation of shading may be produced with crayon on these grained stones just as it would be on grained drawing paper. When the drawing is complete a solution of acid and gum in water is poured or brushed over the stone. By this operation, termed etching, the grease or soap of the crayon is fixed in the stone and at the same time the clear parts of the stone, even the minute spaces between points of the grain, are filled in by the acid gum solution. After the gum has dried the ink or crayon of the drawing may be washed off with turpentine and the gum with water. While the water is still on the stone the image or delineation can be seen by reason of its remaining dry while the other parts hold the water. At this stage passing an ink-charged roller over the stone will bring the roller in contact with the dry parts which will take ink and reproduce the original drawing. The stone is now ready for printing by application of paper under pressure.

The second method is the reverse of this operation. It consisits in etching or gumming the stone first and after the gum has thoroughly dried to engrave or cut through the gum and into the stone, so that wherever the design is cut in, the virgin stone is exposed. After the engraving has been finished the whole surface of the gummed stone is covered with oil, which is rubbed into the engraved lines and allowed to act on the stone for a half hour or less. The stone is protected by the film of gum, except in those places that have been laid bare by the graver and it is just these places that are affected by the grease.

The stone is kept moist while printing ink is rubbed or "daubed" into the engraved lines. On account of their being greased, these lines readily take ink and when properly charged yield impressions on paper that is forced into the lines by pressure. On account of the slowness and difficulty of printing these engraved stones, they are seldom used as plates from which an edition is to be printed. On the other hand, the finest kind of line work, such as maps, script, lettering and in fact all kinds of work formerly done on steel or copper, can be successfully imitated on fine grained lithographic stones.

In order to print this engraved work with commercial economy, the engraving is inked with fatty ink, an impression is taken on starch-coated paper, and this impression is laid down on a smooth, clean stone and the two are brought into close contact by repeated application of pressure. The greasy ink leaves the paper, attaches itself to the clean stone, is treated with gum and acid and a replica of the engraving is thus attained wherein the lines are on the surface of the new stone in place of being depressed, as on the original. This process is the same in principle as that described under the first method, i. e., it is a direct local application of the grease to the clean stone. It differs only in method of application. These transfers, as they are called, are used for power press printing. A further advantage derived from transferring lies in the fact that the design transferred may be repeated on the new stone as often as the dimensions of the design will go into those of the new stone. Thus an octavo plate (6x9½ inches) may be repeated eight times on a 19x24 inch stone and every impression of the latter will yield eight copies of the original engraving. It is principally through this transferring process that stones of large size have lately come into demand. A natural limit to the sizes of the stones is reached when their increased weight and the mechanical difficulty of handling large sheets of paper become factors of economic importance. So it is that stones measuring 42x64x5 inches and weighing about 1,200 pounds are the largest that are in daily use. Indeed even these sizes seem to be almost too large for safe handling so that 36x52 inches is a much more popular size.

It was stated that drawings made on glass could be made to yield a few impressions, but that the image lacked permanency, there being merely an adhesion of the locally applied ink to the glass. Glass is neither porous, nor does it combine, chemically or physically with grease. On the other hand, we found that lithographic stone had the power not only of receiving the image, but also of retaining it. Between these extremes of glass on the one hand and stone on the other come those materials which have found more or less extended use in the lithographic process. Zinc and aluminum are the chief of these substances. Both are inferior to the best stone, taking the quality of the work into account, and especially in the matter of control while in the printing press. Aluminum printing, however, has been brought to such a stage that for some kinds of work it offers economic advantages, such as lightness, cheapness, flexibility (adaptation to rotary presses) over stone, and, on this account, has been a formidable rival of stone printing in recent years. However, for the finest work nothing has been found to equal the best grade of lithographic stone.

The process of practical lithography has been outlined and it is now proposed to consider lithographic stone and the qualities which make it fit for use in the art.

The essentials are chemical composition and texture. Color is a modifying attribute. The following analyses of different stones, each of which has been successfully printed, shows that the chemical constituents may vary considerably, notably the magnesium-calcium ratio. It is to be noted in this stage of our inquiry that the stone should be evenly etched on treatment with cold dilute acid. This will not be possible if the magnesium is

ANALYSES OF KENTUCKY AND BAVARIAN LITHOGRAPHIC LIMESTONE, AND OF STONE FROM MITCHELL COUNTY, IOWA.

	Brandenburg, Ky.*	Solenhofen, Bavaria.*	Mitchell Co., Iowa.†
INSOLUBLE IN HYDROCHLORIC ACID.			
Silica, SiO_2	3.15	1.15	.78
Aluminum-iron oxide $(AlFe)_2O_3$	.45	.22	Trace.
Lime, CaO	.09	Trace.	....
Magnesia, MgO	None.	None.	... .
SOLUBLE IN HYDROCHLORIC ACID.			
Alumina, Al_2O_3	.13	.23	.12
Ferrous oxide, FeO	.31	.26	.....
Magnesia, MgO	6.75	.56	.07
Lime, CaO	44.76	53.80	54.91
Soda, Na_2O / Potash, K_2O	.13	.07	.18
Humus	.....	....	.11
Hygroscopic water, H_2O	.41	.23	....
Water of composition, H_2O	.47	.69	.35
Carbon anhydride, CO_2	43.06	42.69	43.16
Sulphuric anhydride, SO_3	None.	None.	Trace.
Total	99.71	99 90	99.68

* Chemical Laboratory of U. S. Geological Survey.
† Analysis by A. B. Hoen.

present in large proportion. The extent to which the isomorphous magnesium carbonate may replace the lime without affecting the working qualities of the stone, has not been determined. It is really a question of solubility in cold acid and the answer is to be sought by experimenting in this direction. Cold dilute hydrochloric acid, however, will readily etch a very impure limestone when the impurities are mechanical admixtures of silica and alumina. These impurities remain in the solution of calcium chloride as a muddy sediment and the etched surface of the stone will show the roughness due to resistance of these insoluble particles to the acid. Impurities of this kind are very objectionable and, if present beyond a small percentage, unfit the stone for use for fine engraving. Besides the roughness in the etching, they are apt to make the stone uneven in texture, so that the graver would cut unevenly.

The low percentage of silica and alumina in the Mitchell county stone is remarkable and is a decidedly strong point in its favor. The absence of hygroscopic water may be accounted for by the fact of the stone's having been for several months in a warm, dry room. Chemically, the points of difference between the Iowa stone and the German and Kentucky stones, favor the former.

There is a kind of impurity which would not show in analysis, yet is of serious nature when present even in small amount. It is the presence of crystals of calcite throughout the mass of the stone or in veins. Crystalline limestone does not absorb water evenly, nor combine with grease in such a way as to be subject to control. Again, on account of the unequal hardness of the crystals and the matrix, it is not possible to engrave easily and satisfactorily on a stone showing such defects. Calcite is usually confined to veins (faults), but occasionally is developed in the mass of the stone itself. German stones rarely show the latter phase. Of the several samples of Mitchell county stone, those taken from layers above those marked XX in the accompanying illustrations are badly marked, not only with the crystals in the mass, but by numerous marks of interruption in the process of sedimentation. A cross section made perpendicularly to the plane of deposition shows the presence of these irregularities in composition, as well as unevenness in texture.

In the polarising microscope sections taken even from the best layer, show a sprinkling of microscopic crystals of calcite and when these are crowded together they become apparent to the unaided eye as an unevenness in the otherwise unbroken color of the stone.

The best German stone also shows these microscopic crystals of calcite and indeed the whole amorphous groundmass of both the foreign and domestic stones seems to be bound together by this anisotropic medium.

The principal layer, however, is almost free from visible crystalline particles and it is from this layer that the sample stone from which the accompanying illustration was printed is taken.

Lithographic stone should be of even texture, amorphous, free from inclusions of grit and chalk. It should be hard enough to resist the graver to some appreciable extent, yet not so hard as to make engraving difficult. This is a condition that is difficult to describe and cannot be expressed in terms of the common scale of hardness, although it is easily learned after a few trials with a knife point or needle.

The soft stones (yellow of the Solenhofen quarry) are too soft or "chalky" for fine engraving. The dark blue stones, on the contrary, are so hard that the engraver has to apply such force that the effort of holding his tool becomes tiresome and the tool itself quickly loses its point either by wear or by breaking. The hardest stones, however, will carry the finest lines, while similar work on soft stones appears rough and easily wears away. For these reasons stones of intermediate hardness, which embody the good qualities of both the extremes, are most in demand by lithographers and command the highest price. These degrees of hardness are accompanied, in the German stones, by a corresponding variation in color. The soft stones are of a yellow manila-paper tint, the hardest are a blackish gray, while the stones of intermediate hardness are of a grayish buff. So constantly do these colors vary with each other that stones, otherwise perfect, are listed, bought and sold, almost solely on the basis of their color. The Iowa stone is a lithographic anomaly in respect to its color. It is lighter in shade than even the softest of the yellow German stones, yet is of such fine texture and of such comfortable hardness that the engravers who tried it expressed themselves as much pleased with its behavior under the needle point. Of course, the tints of the German stone are the exponents of varying degrees of compactness, which in turn modifies in a direct or indirect way the more or less constantly present percentage of colored impurities. The very small proportion of coloring matter present in the Iowa stone, as compared with the others given in the analyses, affords an explanation of the anomaly above referred to.

As absorption of water is one of the two essential characteristics of lithographic stone, some experiments were undertaken to determine the relative absorbing power of the German and Iowa stone. To do this cubes of the stone were made with faces approximately 2 centimeters square. The surface presented was therefore 24 square centimeters. They were weighed in air and again after immersion in water for twenty minutes with the following results:

Bavarian stone absorbed	.00270	grams.
Iowa " "	.00165	"

The same experiment was repeated, allowing the cubes to remain in water twelve hours. The absorption increased for both as shown below:

Bavarian stone absorbed	.0333	grams.
Iowa " "	0156	"

These figures indicate that the Iowa stone, in spite of its light color, is denser and finer grained than its Bavarian relative. To determine in the case of the Iowa stone whether this absorption, so makedly inferior to that of the German, was sufficient for practical purposes, a slab of the stone about 14x20 inches was tried in the press, the printing being proceeded with in the usual way. No difficulty was experienced in printing an edition of several thousand copies of the work, which was a transfer of finely ruled commercial engraving. The colored illustration accompanying this article was printed from the same stone and it should be stated that the work was undertaken solely to test the printing qualities of the stone and not for any necessity for coloring in the illustration itself. Following up the absorption tests, others were made to determine the specific gravities of the two stones, which were:

Bavarian stone (gray)	2.69
Iowa " (pale cream color)	2.71

These figures accord well with what might be expected from the behavior of the two stones in the tests for absorption.

Lithographic stone is not restricted to any particular geologic age. The Bavarian stone is Jurassic; some from Texas, Cretaceous; from Kentucky, probably Carboniferous, while the stone, for which this comparison is made, is from the Devonian strata of Mitchell county, Iowa.

More significant than age is its mode of occurrence. The German stone lies in nearly horizontal layers, from an inch or two, up to a foot or more in thickness. The aggregate thickness of the strata is 80 feet (Dana). It is not much disturbed from its original position. This is important, as disturbance produces faults and fissures which fill in subsequently with calcite or ferruginous cement, both of which are serious blemishes in an otherwise good stone.

The mode of occurrence of the Iowa stone can be seen in the illustration, Plate VIII. There is considerable variation in the quality of the stone from both the quarries shown. In the Gable quarry the best layer is the one immediately above the floor of the quarry. It is about 2 feet thick. The same stone is shown in the Lewis quarry with the hammer and rule leaning against the fine grained layer. The stone from this layer is apparently homogeneous, in the sample examined, with the exception of the bedding marks. It was noticed in trueing the stone for printing that the surface plane intercepted planes of bedding at small angle and, as these bedding planes always include foreign material, their intercepts with the plane face of the stone would be marked by an outcrop of this foreign material. The bedding planes appear to be not quite as true as in the Solenhofen quarries. Appreciable undulations or pits were noticed in the cleavage surface of the sample. It is hoped that further exploitation of the quarry will yield layers thick enough to be planed for use and at the same time free from checks and calcite inclusions. If layers are found in which the process of sedimentation has gone on uninterruptedly until layers of 2, 3 or more inches in depth have been laid down, there would be little doubt as to the unqualified excellence of the deposit. As Professor Calvin's examination was not carried beyond an observation of the stone exposed on the side of the hill and, as the sample submitted for trial was such a one as he could detach without the aid of a quarryman, there is reason to hope that, as the surface stone is removed, larger and more perfect slabs may be obtained from those portions of the deposit that have not been subject to atmospheric action.

The price of stone varies from 3½ to 17 cents per pound for good quality yellow German stones. The gray stones bring 50 per cent more. A table of the prevailing prices (for yellow stones) and corresponding sizes is given herewith.

Lewis Quarry, southwest of Osage, Mitchell County, Iowa.
× × *Beds of fine grained lithographic stone.*

Gable Quarry, southwest of Osage, Mitchell County, Iowa.
× × *Beds of fine grained lithographic stone.*

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VALUE OF LITHOGRAPHIC STONES.

NO.	SIZE.	Price per pound.	NO.	SIZE.	Price per pound.	NO.	SIZE.	Price per pound.
		Cents			Cents			Cts.
* 1	16x22	3½	13	26x36	8	*25	32x48	13
2	18x24	4½	*14	26x38	9	*26	34x48	13
* 3	19x25	4½	15	28x38	9	27	35x50	14
4	20x26	5	*16	28x40	10	28	36x50	14
* 5	22x28	6	17	28x42	11	29	36x51	14
6	22x30	6	18	29x43	12	*30	36x52	14
7	22x32	6	19	30x40	12	31	40x60	14
* 8	22x34	7	20	30x43	12	*32	40x62	15
9	24x30	7	*21	30x44	12	33	42x60	15
10	24x32	8	22	32x43	12	34	42x62	16
11	24x34	8	23	32x44	12	*35	42x64	16
*12	24x36	8	*24	32x46	12	36	43x64	17

* The sizes marked with an asterisk are those commonly in use.

It is to be noted that for profitable production of lithographic stone there must be facilities for handling and there should be some market for the waste product. As the quarry must be conducted without blasting, the expense of the slower process of gadding or channelling must be taken into account.

For the information of prospective investors the following table of values of lithographic stone imported into the United States from 1868 to 1900, inclusive, is given:

YEAR ENDING JUNE 30.	VALUE.	YEAR ENDING JUNE 30.	VALUE.	YEAR ENDING DEC. 31.	VALUE.
1868	$ 13,258	1880	$ 56,310	1890	$ 105,288
1869	17,044	1881	77,894	1891	107,339
1870	14,225	1882	111,925	1892	107,777
1871	21,311	1883	104,313	1893	91,849
1872	36,146	1884	128,035	1894	74,454
1873	44,937	1885	54,022	1895	107,670
1874	36,902	1886	71,009	1896	74,044
1875	41,963	December 31		1897	58,922
1876	47,101	1887	83,182	1898	60,522
1877	44,503	1888	113,365	1899	86,695
1878	42,700	1889	78,077	1900	94,134
1879	37,746				

In recapitulation it may be stated that the Mitchell County stone is at least as good in quality as the Bavarian stone for lithography in all its branches and it remains to be determined whether or not it can be had in such sizes and at such cost as would warrant its entering the market in competition with the foreign product which has so long been without a rival.

Note. The foregoing tables have been taken from Mr. S. J. Kubel's report on the production of lithographic stone in Mineral Resources of the United States for 1900, U. S. Geological Survey. More complete accounts of the various processes of lithography may be found in Richmond's "A Grammar of Lithography" and in "Die Verfahren des Steindruck's," by H. Weishaupt and others.