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AN EVALUATION OF TRINITY RIVER AGGREGATES OF MARGINAL QUALITY FOR USE IN PORTLAND CEMENT CONCRETE PAVEMENTS

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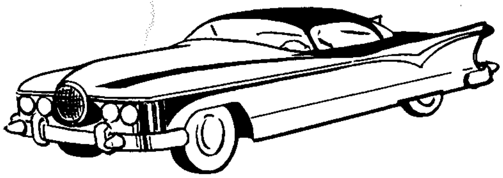

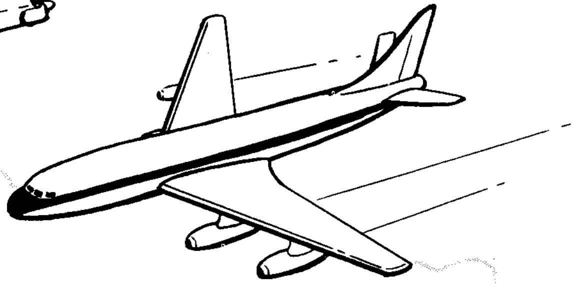

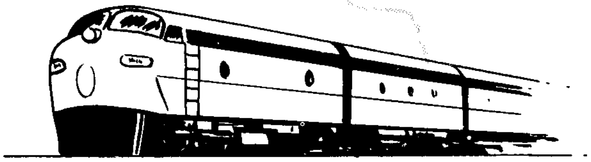

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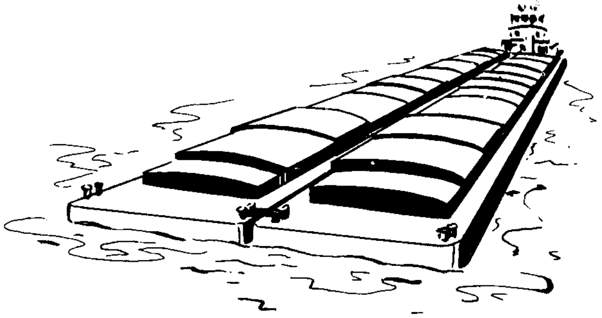

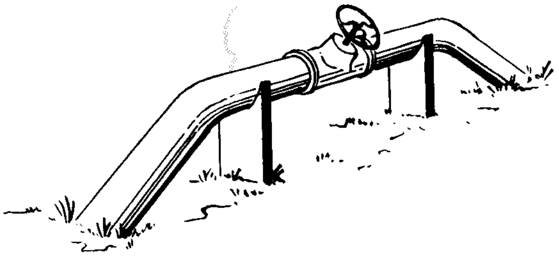

TEXAS TRANSPORTATION INSTITUTE
TEXAS A. & M. COLLEGE SYSTEM
COLLEGE STATION, TEXAS

Project RP-12
Final Report

AN EVALUATION OF TRINITY RIVER AGGREGATES OF MARGINAL QUALITY FOR USE IN PORTLAND CEMENT CONCRETE PAVEMENTS

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Prepared for the Research Committee
of the
Texas Highway Department

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AN EVALUATION OF TRINITY RIVER AGGREGATES OF MARGINAL QUALITY FOR USE IN PORTLAND CEMENT CONCRETE PAVEMENTS

FOREWORD

For many years the Trinity River sand and gravel deposits in the vicinity of Dallas have provided aggregates of excellent quality suitable for making structural concrete of the highest type. Unfortunately, these deposits are being rapidly exhausted. In the same general area, however, there is a large potential supply of concrete aggregates which by certain standards are considered to be of marginal or sub-standard quality. Much of this aggregate, as now produced, passes all the current Texas Highway Department specifications for concrete aggregate. However, pavement concrete made with the aggregate from certain pits will not develop the minimum modulus of rupture (beam-break strength) of 650 psi, as required by the specifications, at normal cement factors. Aggregates from some of the other pits produce marginal strengths and frequently fail to pass.

It was the purpose of this investigation to evaluate these materials that produce concrete of marginal and sub-standard quality to determine the causes for the poor performance and to develop methods for the detection and control of such deleterious material as may be present. These objectives have been accomplished.

In this evaluation the following four sources of material (deposited by the Trinity River near Dallas)* were investigated:

SOURCE	EXPERIENCE RECORD
(1) Keller Pit -	aggregate known to produce pavement concrete of sub-standard quality with usual cement content and consistency.
(2) Fouts Pit -	aggregate produces pavement concrete of marginal quality with usual cement content and consistency.

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* See Appendix A.

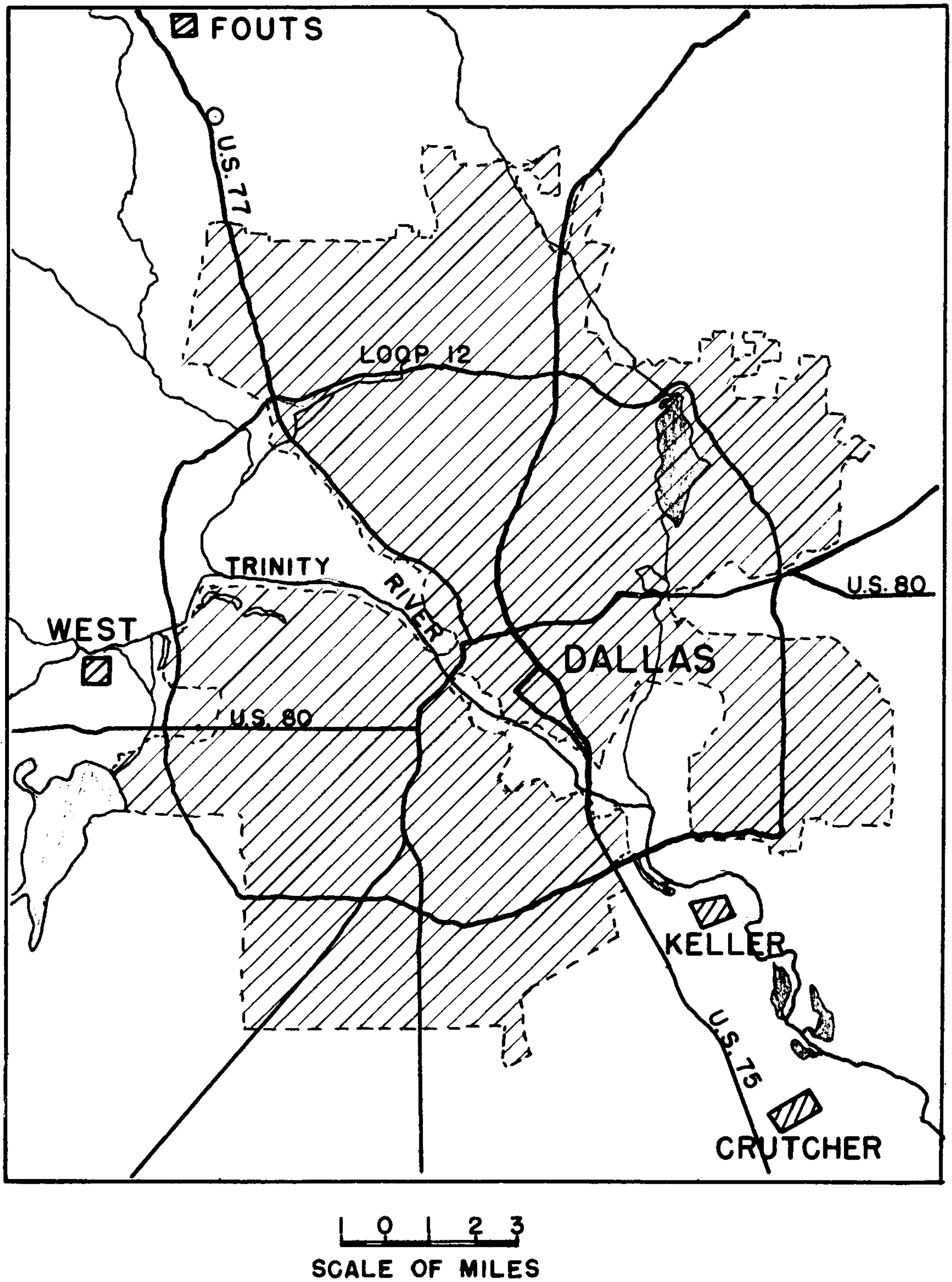

Figure 1. Map of Dallas County Showing location of aggregate pits investigated in this project.

(3) Crutcher Pit - aggregate produces concrete of good quality.
(4) West Pit - aggregate produces concrete of good quality.

The first phase of this investigation was to conduct laboratory tests on the sand and gravel from these four sources in order to determine the particular characteristics, properties, or fractions of the marginal and sub-standard aggregates which could account for their low "beam-break" strengths. Tests were made on the materials to determine their (1) gradation, (2) range of specific gravities (within the various particle sizes), (3) moisture absorption characteristics, (4) resistance to abrasion, (5) soundness, (6) mineral classification, (7) chemical characteristics, (8) strength characteristics in mortars and concretes, and (9) loss by decantation.

The next phase was to determine if the deficiencies of these aggregates could be corrected so that they could produce concrete with satisfactory beam strengths. Finally, a third phase was to develop sufficient information for writing a specification and developing a test to limit and control the use of these marginal and sub-standard aggregates in pavement concrete.

SUMMARY

The aggregates from the Keller and Fouts pits in the Dallas area,which by concrete strength standards are considered to be of marginal or sub-standard quality, were definitely found to have a good engineering and economic potential. These questionable aggregates which have a poor record for developing specified minimum "beam-break' strengths at normal cement factors were found to meet the existing Highway Department specifications for aggregates for use in concrete pavements. Consequently, this investigation indicates that the current specifications and methods of test for concrete pavement aggregates need strengthening. The need for some improvements in certain of the commercial processing procedures used for concrete sands were also revealed.

Tests on the plant processed <u>gravels</u> from the four sources showed that they were all essentially sound, and when used with good clean sand to make concrete, satisfactory "beam-break" strengths could be obtained with normal cement factors. These gravels, and particularly the intermediate size Keller material,

were found to contain a considerable amount of chalk, weak limestone, porous material and flat particles. These undesirable materials can be tolerated in the proportions that now exist but they could prove to be a problem at some future time if the percentage increases appreciably. This deleterious constituent can be detected by a heavy media separation analysis (ASTM C123-57T) and commercial plants can eliminate the undesirable material with a heavy media separation process. It is desirable to specify a maximum percentage of material with a specific gravity less than 2.45 for naturally occurring aggregates, and it is recommended that materials with a good service record be excepted. The service record should include consideration of durability as well as strength development.

Tests on the plant processed sands indicated that the West and Crutcher materials were essentially sound, but that the Keller and Fouts pits had some notable deficiencies. The Keller sand had about 2 to 3% silty-clayey material which was rather firmly attached to the particles. This material is considered detrimental to the bond between the cement paste and aggregate and affected the flexural (tensile) strength directly. The compressive strength and modulus of elasticity were not noticeably affected by this material, since they are only indirectly related to tensile strength.

The presence of this clayey material is attributed to the fact that the aggregate processing plants in the Dallas area do not wash or scrub sand in their usual processing procedure. They do, however, wash and scrub the coarse aggregate. Immediately after separation from the gravel, the sand is dropped into a "sand drag" or "rake classifier" for rinsing, and dewatering with a minimum of turbulence so as to retain an adequate amount of fines. This rinsing procedure is not adequate to clean the detrimental clay material from the Keller sand. When this sand was washed by agitating it in a drum type mixer in the presence of water, which was replaced frequently enough to carry away the impurities in suspension or solution, it produced modulus of rupture strengths considerably higher than the 650 psi specified for pavements. This washing action can be accomplished commercially with either a "revolving scrubber" or a "double screw washer."

It was found that the "Loss by Decantation Test" and the specifications based on its results do not detect, classify, and regulate the deleterious materials in this Keller sand. The "Sand Equivalent Test" (T176-56) as described in the 1958 AASHO Standards does, however, detect the presence of, and classify, this detrimental material satisfactorily.

The Fouts plant processed sand was found to contain a considerable amount of deleterious silts and clays also. In addition, the gradation is not considered to be good in that it contains excessive fines (material passing the #50 sieve in this case). This sand, however, does pass the existing specifications for fine aggregates for concrete pavements. This poor gradation and the presence of the deleterious silt and clay material is largely due to the processing procedure at this pit. After the sand is separated from the gravel on a 1/4" vibrating screen, it is dumped immediately into a large earth "sump" or settling pit. The coarse grained particles which settle rather quickly are dug out by a dragline and stockpiled as washed sand, while the water which runs off carries away some of the suspended and soluble material. The deficiencies of this material could be corrected by using a "revolving scrubber" or "double screw washer" to wash it and a "rake classifier" or "sand drag" to control the amount of fines retained.

The study of the Fouts material tended to point out the rather liberal gradation requirements of the present highway department specifications. If more restrictive gradation requirements such as those of the AASHO were in use, this questionable material could be rejected on the basis of gradation and additional processing required.

RECOMMENDATIONS

This investigation prompted the following recommendations for strengthening the Texas Highway Department's control on natural aggregates for use in concrete pavements:

1. Adopt the "Sand Equivalent Test" to control the relative proportions of detrimental fine dust or clay-like material in fine aggregate. This test was tentatively adopted by the AASHO in 1956 and appears in the 1958 AASHO Standard Methods of Sampling and Testing (AASHO T176-56).

2. Adopt the California Highway Department's requirement for concrete sand, as follows, "an occasional sand equivalent below 80, but not below 75, is acceptable, provided the average of three consecutive samples is 80 or higher."

3. Adopt more restrictive gradation requirements such as those recommended by the AASHO Standard Specifications for Highway Materials (M6-51 and M80-51).

4. Increase inspection and supervision of aggregate processing plants supplying materials to highway contractors. Consider recommending the minimum amount of processing required for aggregates from certain geographical areas or specifying certain limiting procedures for washing, screening, stockpiling, etc.

5. Establish a maximum limit for the proportion of material with a specific gravity less than 2.45 as determined by ASTM Method C123-57T. The specification should apply to all materials that do not have a long-time service record for durability and strength development.

GENERAL

Description of Sand and Gravel Processing

The aggregate materials used in this investigation were obtained from their respective pits on December 3, 1957. All of these pits with the exception of Keller were in operation at that time. In general, the processing of the gravel at these pits was the same, but there were some notable differences in the processing of the sands. In all cases the material was excavated from wet pits by draglines. The amount of overburden which was stripped ranged from 8 to 14 feet at the Keller, Crutcher, and Fouts pits and from 20 to 22 feet at the West Pit. After excavation the material was hauled by truck or bottom dump wagon to a storage pile or hopper. From this pile or hopper the material was fed to a conveyor which carried it to the top of the processing plant on to a scalping screen. The scalping screen separates oversized material (larger than 2" or 3") from the smaller marketable sizes. Material passing the scalping screen falls on a vibrating screen which separates the gravel from the sand (material passing this 3/16" or 1/4" screen). Water from sprays is applied to this screen and is usually used throughout the screening operations on the gravel.

At this point the gravel and sand go in different directions for additional processing. The gravel was thoroughly washed and scrubbed by passing it through log washers. These log washers grind the gravel together in the presence of water which is replaced frequently enough to carry away the impurities in suspension and solution. After washing, the gravel is separated into the desired grading on vibrating screens and stored or stockpiled for use. Gravel processed in this manner will be referred to as PP (Plant Processed) in this report. The sample of Keller gravel used in this investigation was from the "leavings" of a large pile and considerable clay and dirt was dug up with it. This material was further washed and screened in the laboratory before use.

After the sand (material passing 3/16" or 1/4" screen) was separated from the gravel, it received somewhat different processing at the different plants. This material at this stage usually contained considerable silt and clay. At the Crutcher and presumedly the Keller pit this material was dropped immediately into a "sand drag" or "rake classifier" for rinsing and dewatering with a minimum of turbulence so as to retain an adequate amount of fines. After dewatering, the material was stockpiled for future use.

At the West pit the sandy material is first introduced into a large steel settling tank where the water is replaced frequently enough to carry away some of the impurities in suspension and solution. The material settling to the bottom is drawn off by 6" to 8" pipes and dropped into a "sand drag" or "rake classifier" for dewatering and subsequent stockpiling as at the Crutcher and Keller pits.

At the Fouts pit the sandy material passing the vibrating 3/16" or 1/4" screen is dumped immediately into a large earth "sump" or settling pit. The coarse grained particles settle rather quickly and the water which runs off carries away the suspended and soluble material. A drag line continually digs the sandy material from the sump pit and stockpiles it for future use. The sand materials from the different pits, processed as described, will be referred to as PP in this report.

In addition to the PP sands the Keller, Crutcher and West processing plants have huge piles of by-product or waste sandy materials. Since such plants sell considerably more gravel than sand, they usually do not process all of the sandy material separated from the gravel as PP material. Part of this material is carried away immediately after separation and stockpiled as waste. In most cases this material will require additional processing to be suitable for concrete pavements since it will probably contain considerable silt and clay.

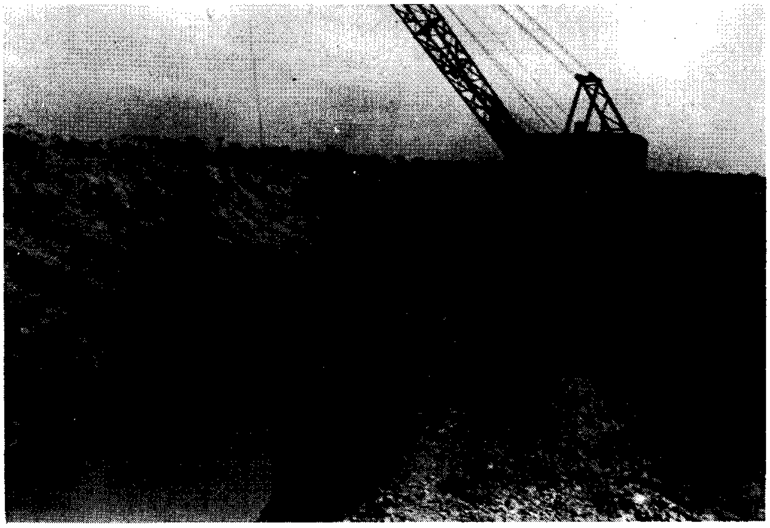

Figure 2. Typical Excavation of Material from a "wet pit." This is West Pit operated by Wesco Material Company in Dallas County.

Figure 3. Typical "Sand Drag" for rinsing and dewatering sand. Crutcher Pit operated by Southwest Construction Material Company in Dallas County.

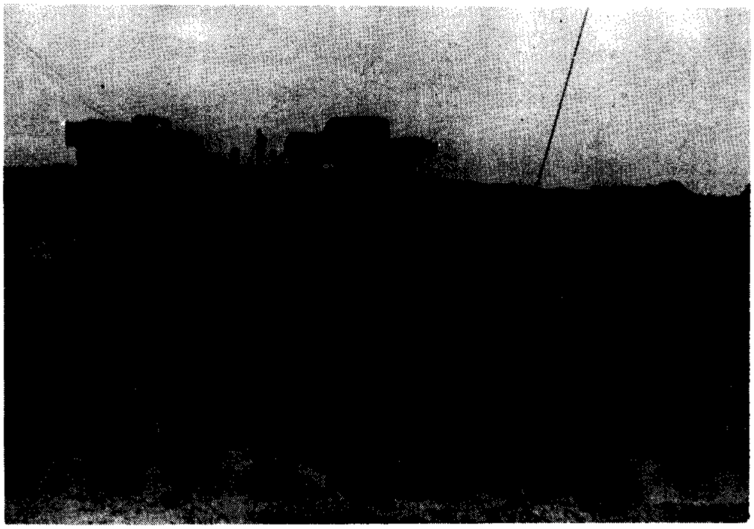

Figure 4. Earth "sump" or settling pit used to dewater sand at Fouts pit operated by Harkrider Gravel Company in Dallas County.

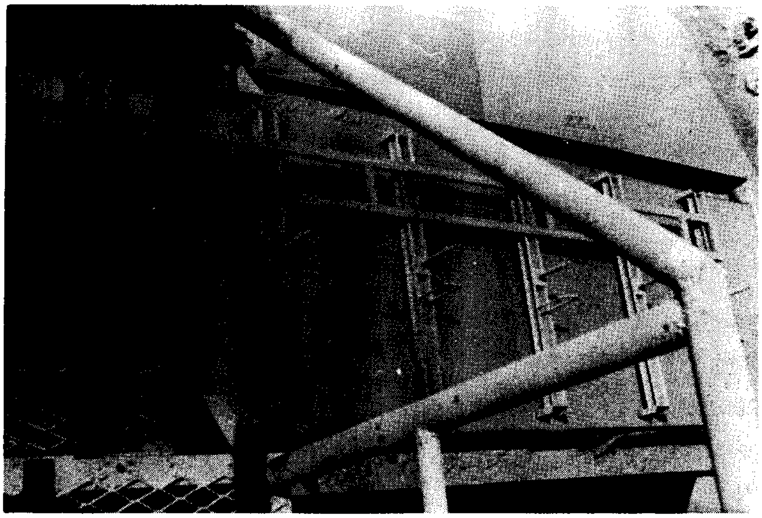

Figure 5. Top view of steel settling tank used to dilute and separate suspended and soluble materials from sand at West Pit operated by Wesco Material Company in Dallas County.

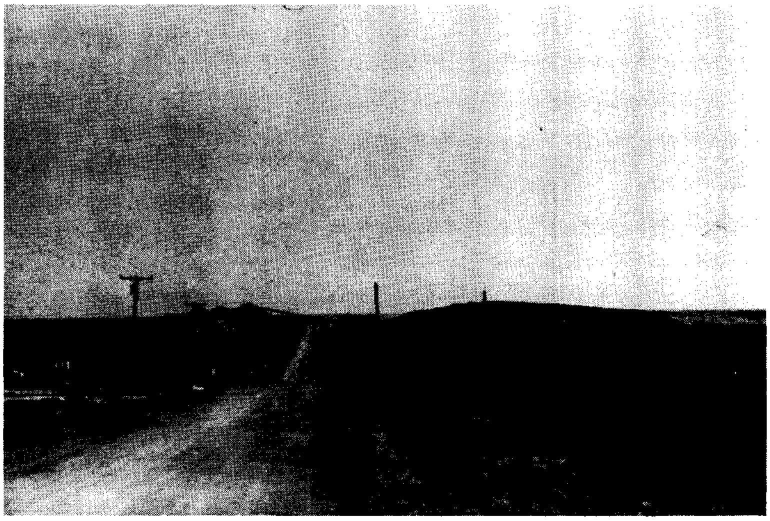

Figure 6. Sand piled to left of road has been processed for use in Concrete. The hugh pile to the right is the sand that is wasted and not processed as concrete sand. Crutcher Pit operated by Southwest Construction Material Company in Dallas County.

Sieve Analysis, Unit Weight and Fineness Modulus

A sieve analysis was performed on the PP sands and gravels from the four sources in accordance with ASTM Standard method of test C 136-46. The results of this analysis were as follows:

GRAVEL

Sieve Size	Percent Passing Crutcher Gravel	Fouts Gravel	Keller Gravel	West Gravel
1"	99	97	89	100
3/4"	88	75	66	85
1/2"	56	48	30	49
3/8"	24	26	13	29
#4	0.4	0.4	1.1	0.8
Fineness Modulus	6.88	6.99	7.20	6.85
Dry Loose Weight (lb./cubic foot)	95	97	94	96

SAND

Sieve Size	Percent Passing Crutcher Sand	Fouts Sand	Keller Sand	West Sand
# 4	100	100	100	100
# 8	91	91	86	84
# 16	78	83	68	72
# 30	54	73	49	54
# 50	12	36	24	22
#100	1.6	3.3	2.6	2.2
#200	0.6	0.4	0.5	0.5
Fineness Modulus	2.63	2.14	2.70	2.66
Dry Loose Weight (lb./cubic foot)	102	103	103	104

Texas Highway Department specifications for gradation requirements of fine and coarse aggregates to be used in concrete pavements are fairly liberal and all of the sands and gravels tested here meet them. However, if these results are compared with the AASHO gradation requirements, which are more restrictive, it is observed that the

Fouts PP sand fails to meet them. These requirements for fine aggregates are as follows:

Sieve Size	Percent Passing
3/8"	100
#4	95-100
#16	45-80
#50	10-30
#100	2-10

The Fouts PP sand has 83% passing the #16 sieve and 36% passing the #50 sieve which indicates that it has an excess of fines. Preliminary strength tests of concrete made with this material indicated it was of marginal or borderline quality. It is felt that removal of some of the material passing the #50 sieve through proper processing, to make this Fouts sand fall well within the AASHO gradation requirement would improve the modulus of rupture strengths considerably. The gradation of the Fouts PP sand is largely due to the present processing procedure of dumping it into an earth sump pit for dewatering. If a "sand drag" or "rake classifier" were used the amount of fines retained could be controlled to some extent and a more uniform quality of product could be produced.

Specific Gravity and Absorption Test

The standard specific gravity and absorption tests described by ASTM method of test C 127-42 and C 128-42 for coarse and fine aggregate respectively were run on the PP gravels and sands. The results of these tests were as follows:

GRAVEL

	Crutcher Gravel	Fouts Gravel	Keller Gravel	West Gravel
Apparent Specific Gravity	2.72	2.74	2.72	2.72
Bulk Specific Gravity (SSD)	2.64	2.68	2.65	2.64
Bulk Specific Gravity (Dry)	2.60	2.64	2.62	2.60
Moisture Absorption (% Dry Weight)	1.7	1.4	1.4	1.8

SAND

	Crutcher Sand	Fouts Sand	Keller Sand	West Sand
Apparent Specific Gravity	2.68	2.70	2.66	2.66
Bulk Specific Gravity (SSD)	2.61	2.64	2.59	2.63
Bulk Specific Gravity (Dry)	2.56	2.60	2.55	2.59
Moisture Absorption (% Dry Weight)	1.8	1.4	1.7	1.6

The bulk specific gravity (Saturated Surface Dry) and percent moisture absorption was used in designing concrete batches. It was anticipated that this data would offer a clue to the particular characteristic or property of the aggregate causing the low "beam-break" strengths. The relatively high moisture absorption of the Keller sand compared to the Keller gravel could possibly be construed to be such a clue indicating the presence of either clay or some porous material. Further tests were run to determine the presence of these materials.

Specific Gravity Analysis

Heavy media separation (HMS) has been widely used in this country to separate gangue from ore and foreign material from coal. Only recently, however, has this method been applied commercially to the production of concrete aggregates. It was felt that these aggregates from the Trinity River near Dallas contained a large quantity of limestone and chalky materials of a relatively low specific gravity which could possibly be classified as deleterious. An analysis similar to ASTM method C 123-57T was performed to determine the distribution by specific gravity of the particles for each aggregate and also to separate the low specific gravity particles for further analysis.

This analysis was accomplished by heavy media separation (HMS) using solutions of various specific gravities. These solutions were obtained by using acetylene tetrabromide (sp. gr. 2.96) and carbon tetrachloride (sp. gr. 1.59) in varying proportions. The results of this analysis were as follows:

GRAVEL

Specific Gravity	Percent Lighter Than (Floating) by weight			
	Crutcher	Fouts	Keller	West
2.7	89	89	97	97
2.6	29	22	24	25
2.5	11	11	10	9.8
2.4	2.9	4.4	4.6	2.2
2.3	0.4	1.5	2.1	1.8

SAND

	Crutcher	Fouts	Keller	West
2.7	92	84	92	87
2.6	5.2	8.0	7.2	9.0
2.5	0.4	0.4	1.2	0.7
2.4	0.1	0.3	0.5	0.2
2.3	0.1	0.0	0.3	0.2

Most of the gravel materials floating on the 2.4 specific gravity were chalk, limestone and porous conglomerate of marine shell and sand. Since the questionable aggregates (Fouts and Keller) had relative high percentages of material lighter than the arbitrary figure of 2.4 specific gravity, the effect of this fraction of material on the modulus of rupture strength was investigated to a considerable extent. Later test results, however, indicated that this material in the above quantities could be tolerated if the sand and gravel were sufficiently clean.

Resistance to Abrasion

The Los Angeles abrasion test was run on the PP gravels from these pits in accordance with the procedure given by ASTM Test C131-55 and the results were as follows:

Percentage of Wear

Crutcher Gravel	Fouts Gravel	Keller Gravel	West Gravel
28	27	27	27

These values are acceptable and indicate that these four gravels are sound in spite of the relatively soft materials like limestone and chalk which are present. Current specifications accept gravel for a concrete pavement with a percentage of wear up to 45.

Soundness

The soundness of these PP materials as determined by the Magnesium Sulfate test (ASTM Test C88-55T) was as follows:

Percent Loss

Crutcher Gravel	Fouts Gravel	Keller Gravel	West Gravel
12	10	5.2	20
Crutcher Sand	**Fouts Sand**	**Keller Sand**	**West Sand**
2.8	3.1	5.1	2.3

These results seem to confirm that the Fouts and Keller gravels are as sound as those from the pits with a satisfactory experience record.

Loss by Decantation

The Texas Highway Department Test (C-11-7) to determine the percent by weight of material loss by decantation was run on the PP sands. The results of these tests were as follows:

Percent Loss by Decantation

Crutcher Sand	Fouts Sand	Keller Sand	West Sand
1.2	1.6	1.9	1.2

These values fall well within the current highway department specification (usually a maximum of 3%) for fine aggregate for concrete pavements.

There are two weaknesses in this method of test, however, which this investigation brought out. First, it is questionable whether sufficient agitation of the sample can be obtained to dislodge clay particles firmly attached to the aggregate. And secondly, there is no way of determining whether the material removed is a deleterious dust, clay, mud, etc., or a very sound mineral material suitable for a fine aggregate or filler. The "Sand Equivalent Test" which is discussed next is felt to remedy these weaknesses.

Sand Equivalent Test

This test serves as a rapid field test to show the relative proportions of detrimental fine dust or clay-like material in soils or fine aggregate. It was adopted in the 1958 AASHO Standard Methods of Sampling and Testing (AASHO T176-56). The California Highway Department requirement for concrete sand is defined as follows, "an occasional sand equivalent below 80, but not below 75, is acceptable provided the average of three consecutive samples is 80 or higher." The average of two tests on each of the four PP sand samples used in this investigation was as follows:

Sand Equivalent
AASHO T176-56

Crutcher Sand	Fouts Sand	Keller Sand	West Sand
91	74	75	86

This test makes a particularly good showing in this investigation

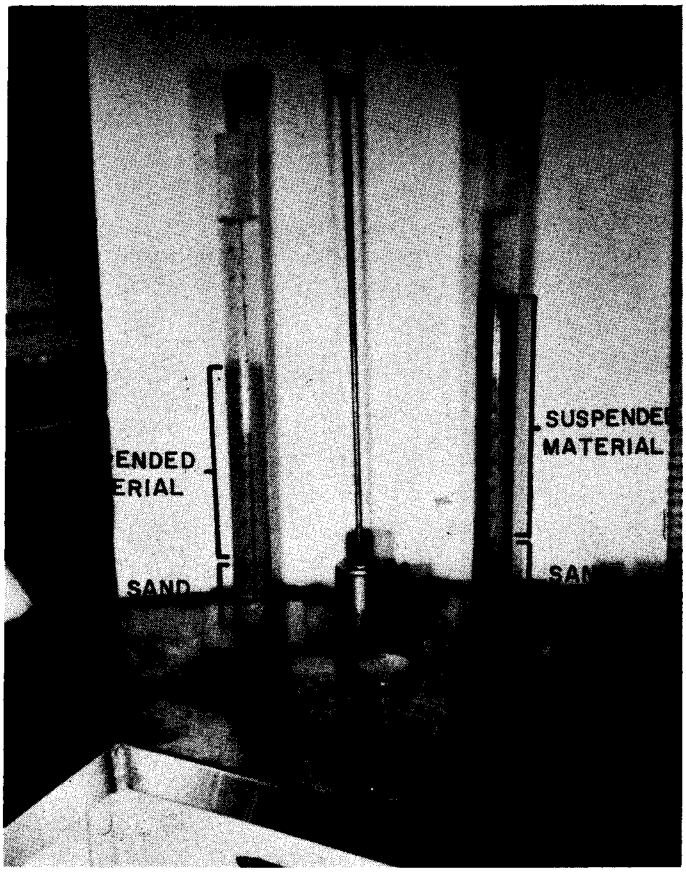

Figure 7. Prepared samples ready for "sand equivalent" determination. Suspended material is deleterious dust and clay. Sound fine aggregate settles to the bottom.

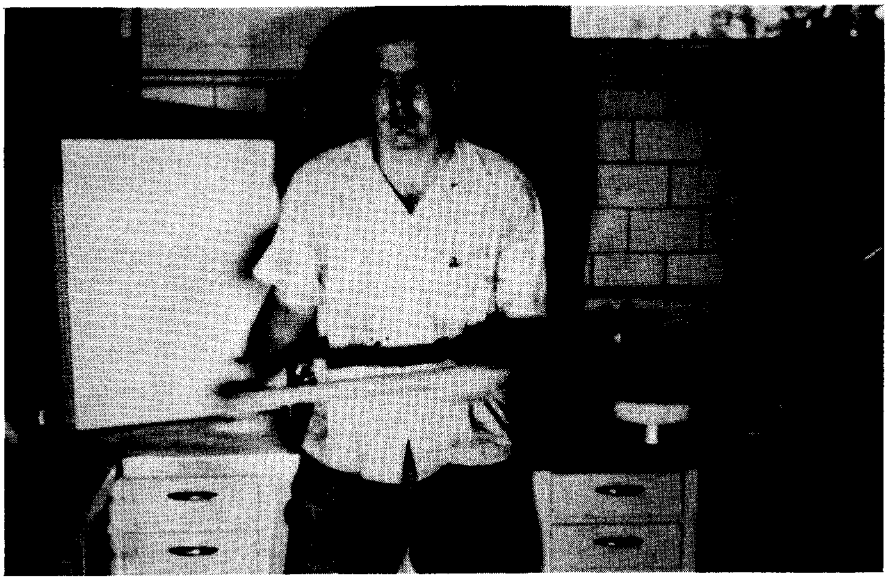

Figure 8. Vigorous agitation of sample for dislodging material firmly attached to fine aggregate. Solution used is a cleansing agent.

since the two questionable materials failed to pass. This test method involves a cleansing agent and considerable agitation to remove fine coatings attached to the particles and experience has shown its ability to indicate the relative proportions of this detrimental fine dust or clay-like material.

When a sample of the PP Keller sand was washed (by agitating it in a drum type mixer in the presence of water which was replaced frequently enough to carry away the impurities in suspension or solution) it gave a sand equivalent value of 92. This water-washed Keller sand made concrete with a modulus of rupture considerably higher than the specified 650 psi for pavements, and also considerably higher than that made with the PP sand (see Figure 12).

Amount of Fines Removed by Washing (Sand)

After studying the results of other tests it was decided to determine how much material could be removed by vigorously washing the PP sands with water and with a detergent. A 500 gm sample of sand was placed in a one-half gallon Mason jar which was approximately two-thirds full of water with 0.1% aerosol added. A cap was placed on the jar and it was shaken and rolled vigorously by hand for two minutes. The contents of the bottle were then poured onto a #200 sieve and rinsed with water. The amount of material in percent passing the sieve is referred to as the amount of fines removed by washing. The results of washing these four PP sands with water and with detergent solution are given below:

Percent Removed by Washing with Water

Crutcher Sand	Fouts Sand	Keller Sand	West Sand
1.2	1.2	2.7	1.1

Percent Removed by Washing with Detergent

Crutcher Sand	Fouts Sand	Keller Sand	West Sand
1.6	2.0	3.1	1.7

These results agree qualitatively with those of the "Loss by Decantation Test," since material finer than a #200 sieve would be held in suspension and lost by decantation. Concrete was batched using water washed and detergent washed Keller sands so the effects of the two different washing procedures on modulus of rupture strength could be observed. Both the water and detergent washed sands produced flexural strengths considerably higher than the PP sand and the specified 650 psi for concrete pavements. The detergent washed sand produced strengths only slightly higher than the water washed sand indicating that this additional effort is probably not justified in this case.

Strength Tests on Concrete (Modulus of Rupture, Compressive Strength, and Modulus of Elasticity)

In this investigation the center point loading modulus of rupture test, standard 6" diam. x 12" cylinder and modified cube compressive strength test (ASTM C116-49), and dynamic modulus of elasticity test (ASTM C215-55T) were used on continuously moist cured specimens. In the modulus of rupture test, both 6" x 6" x 36" beams tested over an 18" span (two breaks were obtained from each specimen) and 3" x 4" x 16" beams with the load applied parallel to the 4" axis over a 14" span were used. Results of tests on the two different size specimens show reasonable agreement (Figure 9). The smaller specimens were used in the more detailed investigations, since more specimens could be tested. The final conclusions, however, were checked by using the larger 6" x 6" x 36" specimens.

Altogether, thirty-four (34) batches of concrete were poured in this study. Twenty-two (22) batches used the Keller aggregate, two batches with each the Crutcher, Fouts, and the West aggregates and six batches used Hearne aggregate for control purposes. One hundred fifty-three (153) 3" x 4" x 16" prism specimens, twenty-four (24) 6" x 6" x 36" prism specimens, and eight 6" diam. x 12" standard cylinders were made and tested. Basically, these batches were designed to determine to some extent the effects of entrained air, removing certain size particles, removing particles of low specific gravity, removing flat or plate-like particles, washing aggregate in water, and washing aggregate with detergent on the modulus of rupture values of Keller aggregate concrete.

At the beginning of this investigation, concrete batches were made with the four aggregates to determine if these samples could be considered representative of the aggregates responsible for the past experience record. The results shown by Figure 9 indicate that they probably were, and also shows a comparison of the results from the different specimen sizes. Figure 10 shows the 28-day compressive strengths and dynamic moduli of elasticity values obtained from these concrete batches. The factors affecting the modulus of rupture do not have the same relative effect on the compressive strength and modulus of elasticity. This is reasonable since flexural strength is a fairly direct measure of the tensile strength of concrete which is governed primarily by three factors: (1) the tensile strength of the cement paste, (2) the tensile strength of the aggregate, and (3) the bond strength between the cement paste and aggregate. While the compressive strength and modulus of elasticity is indirectly related to these factors, they are primarily a function of the shear strength and basic elastic properties of the constituents, respectively.

Physical tests previously made on the aggregates (sand and gravel) indicated that they were all essentially sound and not lacking in adequate tensile strength. The flat plate-like particles and particles of low specific gravity were still felt to be detrimental, however, and were further investigated.

If the low flexural strengths of the questionable aggregates could be attributed to a lack of bond strength, it was felt that the PP sand would be largely responsible, since in all cases it did not receive the washing effort of the PP gravel. To investigate this, concrete batches were made using the four PP sands separately with Hearne gravel as the coarse aggregate. Figure 11 shows the results of the 7-Day modulus of rupture tests on specimens from these batches. These relative values compare favorably with those in Figure 9 and indicate that the detrimental effect could be largely attributed to the sand. Results of the physical tests on the aggregate and additional tests on concrete specimens indicated the above statement to be true.

Further tests on concrete specimens showed that when the PP sand was vigorously washed in water in a revolving drum mixer, the rather firmly attached detrimental material could be removed, allowing greater bond strength between the cement paste and sand to be developed. Figure 12 illustrates the results of such processing and also shows the total effect of washing the aggregate with a detergent and removing certain of the low specific gravity and flat plate-like particles. These particles were removed by putting the gravel into a heavy drilling mud with a specific gravity of 2.45. The low specific gravity and plate-like particles were held in suspension near the surface and were skimmed off. The more dense aggregate was recovered from the bottoms and washed with a detergent solution in a revolving drum type mixer before using in the concrete. Since the water washed aggregate produced very adequate strengths, the additional processing (HMS and washing with detergent) is probably not warranted.

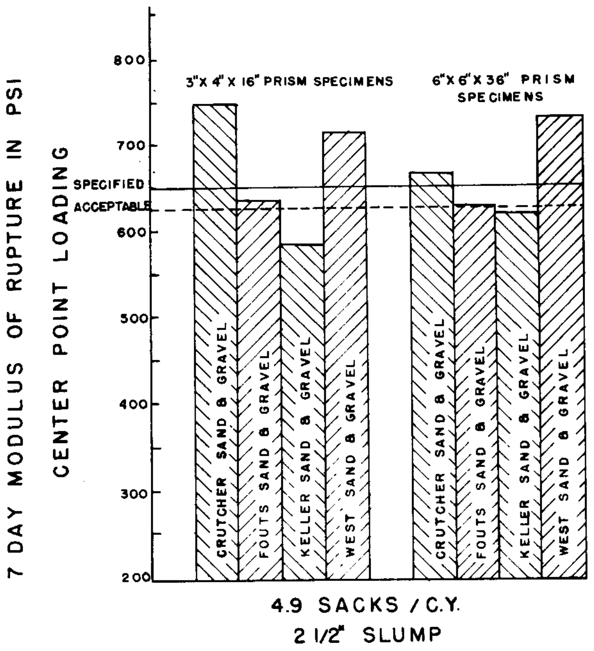

FIGURE 9. COMPARISON OF 7 DAY MODULUS OF RUPTURE STRENGTHS OF TRINITY RIVER PP SANDS & GRAVELS IN CONCRETE

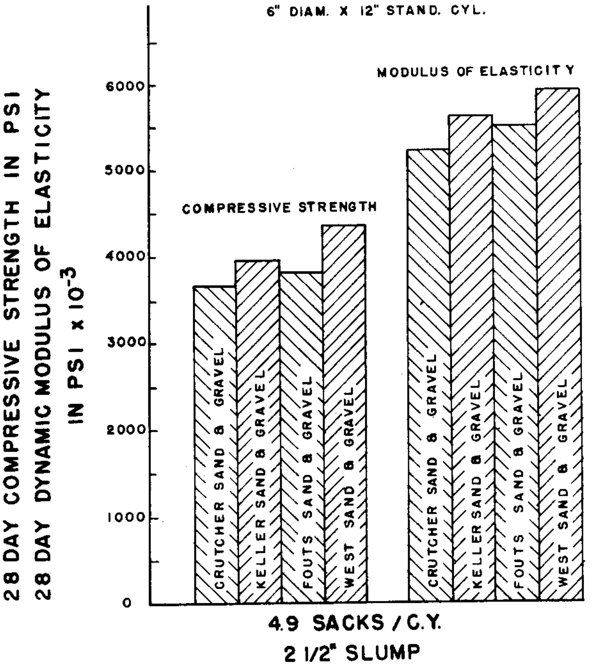

FIGURE 10. COMPARISON OF 28 DAY COMPRESSIVE STRENGTHS AND MODULI OF ELASTICITY OF CONCRETE MADE WITH TRINITY RIVER PP SANDS & GRAVELS

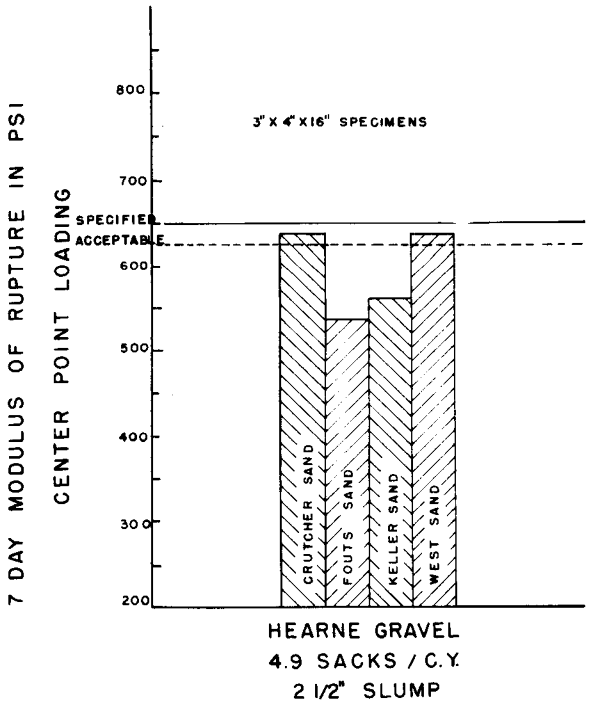

FIGURE 11. COMPARISON OF MODULUS OF RUPTURE STRENGTHS OF CONCRETE USING TRINITY RIVER PP SANDS

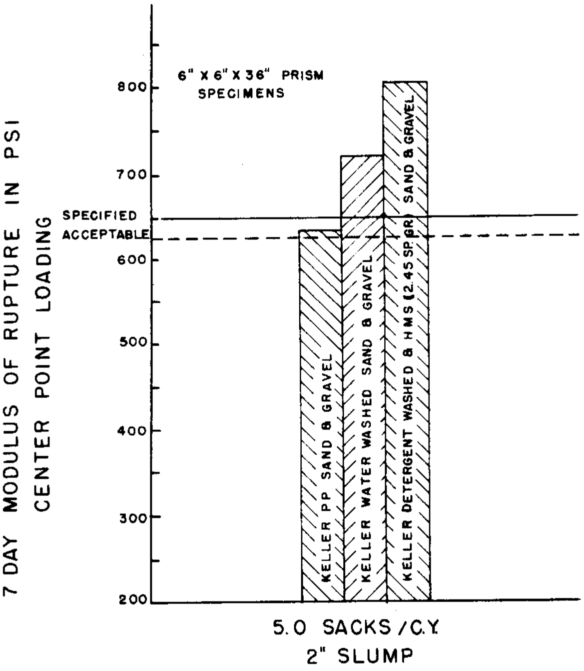

FIGURE 12 EFFECT OF AGGREGATE PROCESSING ON MODULUS OF RUPTURE STRENGTHS OF KELLER SAND & GRAVEL CONCRETE

APPENDIX

APPENDIX A

MISCELLANEOUS INFORMATION ON TRINITY RIVER AGGREGATE PITS INVESTIGATED

1. Name of Source: Keller Pit
   Location: Approximately 2 1/2 miles north of Hutchins on U.S. 75 and 1.0 miles east of U.S. 75, in Dallas County.
   Producer: Southwest Construction Material Company, Dallas, Texas.
   Remarks: Sand and gravel abandoned due to unsatisfactory test results of tensile strength tests made on two paving jobs.

2. Name of Source: Crutcher Pit (also called Keller Pit #2)
   Location: 7 1/2 miles south of Loop 12 near the Hutchins and Fulghum Road.
   Producer: Southwest Construction Material Company, Dallas, Texas.
   Remarks: Sand and gravel was used on concrete pavements of U.S. 75 (South Central from Starks to Grand Avenue) and gave satisfactory beam-breaks.

3. Name of Source: Fouts Pit
   Location: 2.0 miles north of Carrollton on U.S. 77 approximately 700' east of Highway 77.
   Producer: Harkrider Gravel Company
   Remarks: Sand and gravel being used by Austin Road Company on Paving Project on U.S. 75 in Dallas and Collin Counties.

4. Name of Source: West Pit
   Location: 2.0 miles Northeast of Grand Prairie on Myers Road in Dallas County.
   Producer: Wesco Material Corporation, Dallas, Texas
   Remarks: Sand and gravel to be used on 14 miles of paving on U.S. 77 in Ellis County on Waxahachie By-pass.

Supplement to

AN EVALUATION OF TRINITY RIVER AGGREGATES OF MARGINAL QUALITY FOR USE IN PORTLAND CEMENT CONCRETE PAVEMENTS

summarizing information in Appendices B, C, D, E

"How to Provide for Safety in a Laboratory When Using Solutions of Acetylene Tetrabromide, Carbon Tetrachloride, and Ethyl Alcohol in Density Analysis of Concrete Aggregates"

1. Introduction:

Safety in a chemistry laboratory which is well planned and equipped and which is staffed by trained and experienced personnel requires only that the necessary measures be taken by the personnel and that they be constantly aware of all health and safety hazards. However, safety in a highway materials laboratory being used for experiments involving the use of organic solvents and some of the halogenated hydrocarbon compounds requires special attention. This is especially true when these experiments are conducted by personnel more familiar with the testing of concrete aggregates than with the fractional distillation of solutions containing two or more compounds.

2. Heavy Media Separation:

On a commercial basis, heavy media separation is accomplished by using a separation media that is a mixture of a finely ground heavy mineral, such as magnetite or galena, and water. In the laboratory, where preliminary tests are made, the separation media is usually one of the bromine hydrocarbons such as bromoform or acetylene tetrabromide. The specific gravity of these heavy liquids is approximately 2.9. Solutions with densities less than 2.9 are made by adding carbon tetrachloride (Sp. Gr. = 1.56) in varying proportions to the heavy liquid. The purpose of the heavy media separation is to determine the distribution by specific gravity of the particles of an aggregate. The analysis involved the following:

(1) mixing solutions of acetylene tetrabromide and carbon tetrachloride to obtain solutions with several specific densities;

(2) pouring dry aggregate samples in the solution and scooping off what floated;

(3) washing the "float" portion of the aggregate sample with ethyl alcohol three or four times to remove the acetylene tetrabromide and carbon tetrachloride solution;

(4) pouring off and filtering the solution of acetylene tetrabromide and carbon tetrachloride;

(5) washing the "sink" portion with ethyl alcohol usually six or seven times;

(6) oven-drying and weighing the "sink" and "float" portions of the sample;

(7) and, recovery of the acetylene tetrabromide from the wash solution.

Several simple safety precautions were observed to protect the health of laboratory personnel. Adequate ventilation was provided by large fans mounted in the windows; this prevented the accumulation of dangerous fumes. Care was exercised in the use of ethyl alcohol to prevent accidental fire. By carefully washing their hands with alcohol and then with soap and water, the laboratory personnel limited exposure to skin contact by the chemical compounds to a few hours at the longest.

However, the more obscure health and safety hazards involved in the use of these compounds were not properly evaluated until much of the testing was completed. Consultation of several articles and books on hazards in a chemical laboratory has brought to light some of the seriousness of working with certain halogenated hydrocarbons and convinced the laboratory personnel that more care needs to be exercised in their use.

Of course, in the process of testing and developing the proper procedures, some mistakes have been made. These mistakes need not be repeated. Such practices as being careless about spilling the acetylene tetrabromide on the working table, and heating the sand samples containing the carbon tetrachloride and acetylene tetrabromide beyond the temperature at which these organic compounds will decompose were not repeated, at least in the same way. Experience is an effective teacher, even if costly at times.

3. Specific Information About the Chemicals Used Which Affect Health and Safety Standards in a Laboratory Where Heavy Media Separation is Being Conducted:

Of the three organic compounds used in heavy media separation, the acetylene tetrabromide is the one which requires the most attention to its use if the necessary health and safety standards are to be achieved. Listed in Table I are some of the health and safety risks associated with the use of acetylene tetrabromide as well as the other two compounds involved.

Table I

SOME HEALTH AND SAFETY RISKS ASSOCIATED WITH THE USE OF CERTAIN ORGANIC COMPOUNDS

Is this compound:	Acetylene Tetrabromide	Carbon Tetrachloride	Ethyl Alcohol
(1) inflammable	No	No	Yes
(2) volatile	Slight	Yes	Yes
(3) toxic --			
a - if vapor is inhaled	Yes	Yes	No
b - if taken internally	Yes	Yes	No
(4) a lachrymator	No	No	No
(5) a vesicant	Mild	No	No
(6) a skin irritant	Yes	Yes	No
(7) corrosive to --			
a - metals	*Yes	No	No
b - cork	Yes	Yes	Yes - in vaporized form
c - glass	No	No	No
d - paper	No	No	No
e - rubber	Yes	Mild	Yes
f - glazed porcelain	No	No	No
(8) sensitive to light (needs protection from direct sunlight) (tends to decompose in direct light)	Yes	Yes	No

---

* Acetylene tetrabromide is highly corrosive to most metals, especially at elevated temperatures; porcelain or glass containers are suggested.

This information is taken from several sources, all of which are listed in the bibliography at the end of this report. It will be noted that the properties of acetylene tetrabromide which require attention in providing for the protection of health and safety are: (1) it is a skin irritant, (2) it is highly corrosive to metals, and (3) it is sensitive to light.

The fact that acetylene tetrabromide is a skin irritant is complicated by the fact that it is not miscible in water, but rather is oily; therefore, it is not easily removed from the skin. However, this compound is soluble in alcohol and, if it is removed carefully with alcohol, soap and water will clean the skin. The insolubility of acetylene tetrabromide in water, or soap and water, indicate that it must be used carefully to prevent clothes from being contaminated; this could lead to overexposure and skin irritation if care in the use of this compound is not exercised.

Acetylene tetrabromide is highly corrosive to most metals, especially to aluminum, magnesium, lead and zinc. The Dow Chemical Company, which is one of the companies producing acetylene tetrabromide, states that "steel is a satisfactory material of construction for use with Acetylene Tetrabromide under normal conditions."[1] However, most of the authors of books on safety in the use of halogenated hydrocarbons recommend the use of glass or porcelain containers with acetylene tetrabromide. Incidentally, carboys shipped from Dow are made of glass.

Acetylene tetrabromise is sensitive to light and continued exposure to sunlight, especialy, favors decomposition. The danger from this property is not great, however, and proper protection can be provided by storing the container of acetylene tetrabromide in a reasonably dark closet, in colored containers, or by placing the container in a properly marked wooden box.

Health and safety hazards pertaining to the use of carbon tetrachloride in heavy media separation in a laboratory are a result of the toxicity of the fumes and the fact that carbon tetrachloride is rather highly volatile. The American Standard, "Maximum Acceptable Concentration of Carbon Tetrachloride," prepared by the American Standards Association, limits the concentration in the atmosphere to 25 parts per 1,000,000 by volume and says, further, that the vapors of carbon tetrachloride do not become detectable by odor to most persons until the concentration is approximately 70 ppm. A copy of part of this American Standard appears in the appendix to this report.

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[1] "Product Information, Acetylene Tetrabromide: $CHBr_2$," page 2; The Dow Chemical Company, Midland, Michigan.

The fact that the maximum allowable concentration is about one-third of the minimum concentration detectable by odor indicates the seriousness and importance of providing proper safety measures. In laboratory practice adequate cross ventilation will be sufficient. However, it appears that laboratory experiments involving the use of carbon tetrachloride should be performed under a ventilated hood rather than depending upon cross ventilation for the prevention of dangerous concentrations of the fumes.

Carbon tetrachloride is also subject to decomposition in the presence of strong light and should be stored in a dark closet. Carbon tetrachloride is a skin irritant, also, but it is more easily removed than is the acetylene tetrabromide. Washing sufficiently to remove the acetylene tetrabromide will also remove the carbon tetrachloride.

The dangers associated with the use of ethyl alcohol are attendant to its inflammability. Strict attention to preventing the use of alcohol in situations where ignition is likely will provide for adequate protection. One further precaution is related to the fact that alcohol, like some other organic solvents, causes rubber to expand and harden and cork to deteriorate. Glass containers with ground glass stoppers are the most satisfactory for alcohol.

Excerpts from several sources which are pertinent to the subject of providing for adequate health and safety measures necessary in the use of these compounds are appended to this report.

4. Suggested Laboratory Precautions:

Several easily applied practices, some of which are almost universally adhered to in good laboratory procedure will insure both health and safety in a laboratory where organic compounds are used. These are as follows:

A. While handling and storing:

1) Use pyrex containers with ground glass stoppers for storing purposes and identify the contents of all containers with durable labels.

2) Keep containers in a cool, dark, well-ventilated closet.

3) Inspect all shipping containers immediately upon arrival for leaks. Replace if necessary.

4) Remove from the shipping container only the quantity which is needed at the time. Clean carefully and completely any spilled liquid (this could be the source of future contamination, especially if the liquid is acetylene tetrabromide). Keep Spilled Liquids To A Minimum.

B. While doing heavy media separation:

1) Handle liquids carefully.

2) Avoid spilling liquids.

3) Avoid skin contact when possible.

4) Keep containers (beakers, jars, funnels) clean.

5) Wash hands and any other area of skin in contact with the liquids carefully at least once an hour or when through with part of the experiment.

6) Wash all empty containers at end of the day. Do not leave contaminated containers overnight without washing.

7) While drying samples, do not heat to a temperature which will cause residual acetylene tetrabromide to decompose. (239° - 242°C).

8) Avoid excessive expsoure to fumes from a container of carbon tetrachloride. (Keep bottle tightly closed.)

9) Avoid placing acetylene tetrabromide or sand sample containing acetylene tetrabromide in a metal container. Use glass beakers for floating and washing samples and cardboard containers for storing samples (1 pint ice cream cartons serve satisfactorily).

C. While recovering the compounds from the wash solution:

1) Observe all precautions mentioned previously.

2) Use recovery apparatus with ground glass joints and connections which are properly secure and do not allow vapors to escape to the atmosphere.

3) Do not allow any of the liquids to come in contact with metal, rubber, or cork.

4) Observe the operating temperature and pressure of the distillation apparatus and control them closely.

5) Avoid skin contact when possible.

6) Do not breathe fumes escaping from the recovery system, especially when the system is heated.

7) Avoid haste in the recovery process.

8) Be familiar with all parts of the recovery apparatus before using.

APPENDIX B

GUIDE FOR SAFETY IN THE CHEMICAL LABORATORY

Prepared By And Published For
THE GENERAL SAFETY COMMITTEE OF THE
MANUFACTURING CHEMISTS' ASSOCIATION, INC.
Washington, D. C.

Second Printing

D. Van Nostrand Company, Inc.
New York

FOREWORD

The Manufacturing Chemists' Association subscribes to the maxim that:

"Chemicals in any form can be safely stored, handled, and used if their hazardous physical and chemical properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed."

To implement this principle, the management of every unit within a manufacturing establishment must give wholehearted support to a well integrated safety policy. The importance of management interest cannot be overemphasized, because employees take their cue from "the boss" on matters of safety as on other plant business.

Once management accepts this responsibility, its principal problem is to determine the best method of disseminating safety information throughout its organization. One of the constructive measures by which the Association has advanced uniform safety standards is the publication of Chemical Safety Data Sheets. There is little doubt that this effort contributed to the knowledge and understanding of the hazards of chemicals and improvement of their safe handling throughout the industry. One of the principal contributions to general safety is the coordinated effort by all technical committees.

Chapter I

GENERAL RULES FOR LABORATORY SAFETY

The persons in charge of chemical laboratories should be safety minded. Their attitude toward fire and safety standard practices in invariably reflected in the behavior of their entire staff, because laboratory personnel are prone to emulate their supervisors.

Thus key men should:

1. Bear full responsibility for maintaining the highest standards of safe working conditions.
2. Provide safeguards against hazardous undertakings.
3. Educate their supervisory staffs to be alert to all hazards.

No general set of rules can ensure safety. Safety results from an attitude of mind and depends upon the effort of each individual to eliminate all unsafe conditions and acts that give rise to accidents. Positive action closes the door to potential dangers and reduces accidents to a minimum.

A safety program is only as strong as the worker's will to do the correct things at the right time. The fundamental weakness of most safety programs lies in too much lip service to safety rules and not enough action in putting them into practice.

Safety practices should be practical and enforceable. Management should avoid the tendency to place the blame for accidents on individuals, because many times the basic cause is its failure to select and train competent supervisory personnel and encourage the establishment of safe practices and working conditions.

Accident prevention is based on certain common standards of education, training of personnel, and provision of safeguards against accidents. To meet these standards, every laboratory should have:

1. A staff composed of safety-minded individuals.

2. A capable safety staff consisting of a safety group or committee, the leader or chairman of which should be the head of the laboratory or another person of substantial responsibility.
3. An educational program to promote safety and fire prevention.
4. Proper supervision of all work in various divisions of the laboratory by experienced men.
5. Regular inspection program of all working areas.
6. Corrective discipline for unsafe practices of laboratory personnel.
7. Adequate safeguards against physical exposure to hazardous chemicals and equipment.
8. A policy of encouraging the use of personal protective equipment, such as suitable clothing, eye protection, face shields, masks, etc.
9. First-aid facilities including competent personnel.
10. Complete records of all accidents for periodic computation of accident frequency and severity rates and for purposes to determine the causes of accidents and means of prevention.

As a result of operations and materials-handling problems peculiar to the chemical industry, members of the Manufacturing Chemists' Association have found it desirable to stress certain phases of their safety programs. Much emphasis is placed on such phases as:

A. Employee training in first-aid measures for exposure to chemicals.
B. Periodic testing and inspection of pressure vessels and pressure relief devices.
C. Requirement of written permits for performing flame-producing work (welding or cutting) in locations where flammable liquids are stored or used.
D. Requirement for written permits authorizing vessel entry especially where the equipment has contained flammable, corrosive, or toxic materials.

E. Requirement that, during all hazardous operations involving flammable, toxic, or detonable materials, one or more individuals shall be within reasonable communicable distance of the operator.

F. Disposal of chemical wastes. In many instances, a separate department is established to handle technical and engineering aspects of this problem. The problem is particularly close to chemical plant operation, and control measures are often correlated by engineering and safety personnel.

The accompanying chart blueprints the safety organization in the typical well-run chemical plant. As mentioned previously, the principles outlined above and incorporated into the chart are not unique with the chemical industry. Proper application of these principles in MCA member organizations has resulted in favorable industry-wide accident prevention experience. The organizational chart assumes the existence of safety committees, because committees have found to be the most effective means of accomplishing the desired goal — enlisting each employee's personal effort toward preventing accidents.

Chapter VI

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FLAMMABILITY

Flammable Materials

Whenever a new chemical is synthesized or isolated, or a novice comes in contact for the first time with any flammable chemical, the potential danger of fire exists. It is therefore essential that chemical and physical properties of new materials be determined, those of other chemicals be studied and well understood.

In the case of a known product, textbooks, handbooks, or other references will give the essential information required for determining the proper safety precautions to be taken. However, for a new chemical all requisite properties must be determined in routine laboratory procedure.

The following facts should be known for the safe handling of a given chemical:

1. Physical state of the product. Is it a liquid, solid, aqueous solution, or gas, and under what conditions?
2. Physical characteristics. Is it vaporizable? What is its vapor pressure, boiling point, etc.?
3. Explosive limits, both upper and lower, in per cent by volume in air.
4. Flashpoint (closed cup, open cup, or both).
5. Chemical reactivity (acid, alkaline, or oxidizing).
6. Is product shock sensitive (detonable)?
7. What conditions or chemical contaminants can cause product to become dangerous?
8. Ignition temperature.

One of the foremost guides to the physical properties of flammable substances in their relation to fire hazards is the tabulation of known properties of several hundred products (NFPA 325, 1951 Edition, of the National Fire Protection Association[1]).

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[1] The National Fire Protection Association was organized in 1896 to promote the science and improve the methods of fire protection and prevention, to obtain and circulate information on these subjects and to secure the cooperation of the public in establishing proper safeguards against loss of life and property by fire.

PHYSICAL AND CHEMICAL PROPERTIES OF SELECTED ORGANIC COMPOUNDS

Compound	Formula	Molecular Weight (to nearest 0.01)	Density gm/ml (to nearest 0.01)	Boiling Point °C
Acetone	CH_3COCH_3	58.08	0.79	56.5
Acetylene Tetrabromide	$CHBr_2CHBr_2$	345.70	2.96	*151^{54}, 119^{15} d. 239-2-42
Butyl Alcohol	$CH_3(CH_2)CH_2OH$	74.12	0.81	117.71
Carbon Tetrachloride	CCl_4	153.84	1.60	76-77
Ethyl Alcohol	CH_3CH_2OH	46.07	0.79	78.3

*NOTE: Acetylene tetrabromide boils at 151° C with an absolute pressure of 54 mm. of mercury, and at 119°C with an absolute pressure of 15 mm. of mercury. These two pressures (54mm. Hg, 15 mm. Hg) indicate that a vacuum is applied to the compound as it boils. Acetylene tetrabromide decomposes at atmospheric pressure when heated to 239° - 242° C.

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Acute and Chronic Toxicity

Chemicals will show a greater or lesser difference in toxicity depending upon whether they act upon the body for a short time or a long time. Thus two substances may have nearly identical degrees of toxicity (equal potency) when inhaled for a single period of time or when swallowed once. Their potency, however, may be greatly different when they are inhaled or swallowed every day for a long period of time. In addition, the nature of the toxic injury produced by a chemical can be quite different depending upon the duration of exposure.

Acute toxicity is defined as that which is manifest on short exposure. "Short exposure" cannot be defined precisely; it is commonly thought of as a single oral intake, a single contact with the skin and eyes, and a single exposure to contaminated air lasting for any period up to about 8 or possibly 24 hours.

Chronic toxicity is defined as that which is manifest when the toxicants act upon the body over a long period of time. The time period and the pattern of exposure cannot be stated precisely; ordinarily they are thought of as regular daily exposures for periods measured in weeks, months, and even years. Some substances — radium, for example — can produce a chronic poisoning after a single dose has been swallowed, because excessive amounts are retained in the body for many years. Other substances must be encountered repeatedly for long periods of time before chronic effects result. Regardless of the exact pattern, chronic toxicity is manifest when the toxicant acts upon the body over a long period of time without significant respite.

Types of Exposure

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There are but four types of exposure to chemicals: (1) contact with the skin and the eyes; (2) inhalation; (3) swallowing; and (4) injection. These are listed in order of importance in chemical work.

INDUSTRIAL HYGIENE AND TOXICOLOGY

Editor: Frank A. Patty
Publisher: Interscience Publishers, Inc., New York

1,1,2,2, - TETRABROMOETHANE (Acetylene Tetrabromide)

1. Source

Tetrabromoethane ($CHBr_2CHBr_2$) is prepared by the action of bromine and acetylene.[30]

2. Uses and Industrial Exposures

In microscopy; solvent for fats, oils, waxes; separating minerals by density.

3. Pertinent Chemical and Physical Properties

Physical state: yellowish liquid
Molecular weight: 345.70
Specific gravity: 2.9536 at 25°/4° C.
Melting point: 0.13° C.
Boiling point: 239-242° C.[30]
Vapor density: 11.92 (air = 1)
Refractive index: 1.637951 at 20° C.
Solubility in water: 0.0651 g./100 g. water at 30° C.[28]
Miscible with ethyl alcohol, ether, chloroform[28]

1 mg./l. ≈ 70.7 p.p.m. and 1 p.p.m. ≈ 14.14 mg./cu.m. at 25° C., 760 mm.

4. Physiological Response

See Table 38.

TABLE 38

PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF TETRABROMOETHANE — DOGS[27]

Concentration		Response
mg./l.	p.p.m.	
300	21,000	An exposure for 50 min. caused narcosis after 1/2 hr. Repeated in a day caused death after 24 hr.

36	2,560	Shortness of breath, vomiting, increasing ataxia and finally death after 5 days
18	1,280	
9	640	

5. Odor

Similar to camphor and chloroform.

APPENDIX C

THE DOW CHEMICAL COMPANY

PRODUCT INFORMATION

ACETYLENE TETRABROMIDE

$CHBr_2CHBr_2$

Synonym: 1,1,2,2, Tetrabromoethane

I. General Description

Acetylene Tetrabromide is a clear, colorless liquid with a mild sweet odor. It is one of the heavier organic liquids having a density nearly three times that of water. Its uses generally depend upon this high density.

II. Properties and Specifications

A. Properties

Molecular Weight	345.7
Specific gravity at 25/25° C	2.955-2.965
Pounds per gallon at 25°C	24.57
Boiling Point at 15 mm. Hg.	119°C
Decomposes at 760 mm. Hg.	239-242°C
Freezing Point	-1°C ± 1°
Fire Point	None
Flash Point	None
Latent Heat of Vaporization at 60°F	-83.2 B.T.U./lb.

Viscosity 77°F	9.269 cps.
100°F	6.575 cps.
160°F	3.27 cps.

B. Coefficient of Thermal Expansion in Ft^3/ft^3/°F

50-68°F	.000413
68-86°F	.000416
86-104°F	.000419
104-122°F	.000423

C. Vapor Pressure vs. Temperature

°F	mm. Hg.
149	1
204	5
230	10
258	20
291	40
311	60
337	100
378	200
423	400
470	760

D. Solubility, gms./100 gms. solvent at 77°F

Acetone	∞
Benzene	∞
Carbon Tetrachloride	∞
Chloroform	∞
Ether	∞
N-Heptane	103
Water	<1

E. Specifications

Specific Gravity	2.955-2.965
Acetylene Tetrabromide, not less than 98%	
Freezing Point	-1° C ± 1°
pH (Water extract 1:1 by volume)	5.0-7.0
Color (APHA) Max.	100

III. Toxicity

A. The vapor concentrations of Acetylene Tetrabromide at ordinary room temperatures are not sufficient to be a toxic hazard. However, if Acetylene Tetrabromide is to be used in an open container where the vapors would have a chance to escape into the room, it is suggested that a hood be placed above the container to draw away the fumes.

B. Acetylene Tetrabromide is toxic if taken internally, however, in the normal uses of this product the hazard of oral ingestion is not of practical significance.

C. Acetylene Tetrabromide if confined in contact with the skin for a prolonged period of time will produce a skin irritation. Experience, however, has shown that there is little danger of irritation if any material spilled on the skin is promptly removed with soap and water.

IV. Stability

A. Acetylene Tetrabromide is subject to decomposition under conditions of excessive heat. It is not recommended for use above 180°F. Exposure to direct sunlight and the presence of acid or moisture will promote decomposition.

B. The decomposition products will cause corrosion of some metals. The use of aluminum, magnesium, lead, and zinc with this product should be avoided. Steel is a satisfactory material of construction for use with Acetylene Tetrabromide under normal conditions.

C. Acetylene Tetrabromide is not recommended for use with plastics or synthetic rubbers.

V. Uses

A. Balancing Fluids

Acetylene Tetrabromide becuase of its high density is of value as a balancing fluid and vibration dampener for use in conjunction with various centrifugal-type machines.

B. Gauge Fluid

It is widely used in many industries as a gauge fluid in manometers and liquid level type gauges.

C. Gravity Separation Fluid

Acetylene Tetrabromide is used as the heavy liquid media for the sink-float separation of special minerals. It is also used in the same manner as one of the liquids in a gravity method of mineral analysis. Industrially, this same principle is used for separations, as examples the separation of scrap metals and the separation of defective parts from satisfactory parts.

D. Solvent

Acetylene Tetrabromide can be used as a solvent for a number of fats, waxes, and oils.

VI. Packing

	Net	Gross
Carboys: 5-gallon	125	161
Cases: (4 one-gallon bottles)	100	138
Bottles: 1-gallon	25	38

ASA
Reg. U.S. Pat. Off.
Z37.17 - 1957
UDC 613.63

APPENDIX D

American Standard

MAXIMUM ACCEPTABLE CONCENTRATION OF CARBON TETRACHLORIDE

1. Scope and Purpose

1.1 The maximum acceptable concentration of carbon tetrachloride applies to all places of employment.

1.2 The purpose of the standard is to prescribe the maximum acceptable concentration of carbon tetrachloride in the atmosphere of work places for guidance in design and operation so as to protect the health of workers.

2. Properties of Carbon Tetrachloride

2.1 General Properties. Carbon tetrachloride or tetrachloromethane is a colorless nonflammable liquid with a sweetish odor. Its vapor is approximately five times as heavy as air. It is used extensively as a solvent for different materials, as fire-extinguishing agent, and in dry cleaning and degreasing operations.

2.2 Physical-Chemical Properties*

Chemical Formula	CCl_4			
Molecular Weight	153.84			
Specific Gravity	1.5941 at 20/4C (1.6326 at 0/4C			[1]
Freezing Point	—22.9 C			[1]
Boiling Point	76.75			[1]
Vapor Pressure				
O C	10 C	20 C	30 C	[1]
33 mm	56 mm	91 mm	143.0 mm	
Solubility	0.080 parts in 100 parts of water at 20 C; miscible with alcohol, ether, and benzene			

Carbon tetrachloride is not decomposed by cold sulfuric acid nor by strong nitric acid.

In contact with an open flame or a hot object, as a hot electric heating plate, or in an electric short circuit, the vapors of carbon tetrachloride may form phosgene, chlorine, and hydrochloric acid, which are toxic substances [2-3]. The irritant odor of hydrochloric acid and chlorine will give warning of such decomposition of carbon tetrachloride and should be considered as indicative of inadequate ventilation.

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* Numbers in brackets throughout the text refer to corresponding numbers in References on page 9.

2.3 Toxic Properties. In high concentration, carbon tetrachloride has narcotic properties similar to chloroform. Symptoms such as nausea, vomiting, and headache are experienced by some people at low concentrations. Liver and kidney damage may be produced by exposures which produce no or little symptomatic disturbances during exposure. The ingestion of carbon tetrachloride may cause severe and possibly fatal poisoning depending on the dosage and other factors. The vapors of carbon tetrachloride become detectable by odor to most persons at a concentration of about 70 ppm. The contact of carbon tetrachloride vapors with mucous membranes will produce a burning sensation. The prolonged or repeated contact of liquid carbon tetrachloride with the skin causes in some instances burning and stinging sensation, erythema and hyperemia, wheal formation, and later vesicular eruptions. It removes the protective fat of the surface of the skin and renders the latter dry and prone to cracking, opening the way to secondary infections. The toxicity of carbon tetrachloride is considerably enhanced by the ingestion of even moderate amounts of alcohol.

3. Maximum Acceptable Concentration

3.1 The maximum acceptable concentration of carbon tetrachloride shall be 25 parts per 1,000,000 parts of air by volume, corresponding to 0.157 mg per liter at 25 C and 760 mm Hg for exposures not exceeding 8 hours daily with the understanding that variations should fluctuate around 10 ppm.

3.2 This value is based on experimental observations with various species of animals [4] and on comparison of air analyses with clinical observations in operations where carbon tetrachloride was handled.

APPENDIX E

THE ANALYTICAL CHEMISTRY OF INDUSTRIAL POISONS, HAZARDS AND SOLVENTS

By: Morris B. Jacobs, Ph.D.
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4. Carbon Tetrachloride

This chlorinated solvent is used as a degreaser for metal parts, as a cleaning agent in dry cleaning, in the extraction of fats, as a solvent for crude rubber, lac, resins, etc.; in the vulcanization of rubber, in fire extinguishers, as a component of insecticide sprays and soap solutions, as a delousing agent, as a dry hair shampoo and as an anthelmintic drug for it is almost specific against hookworm.[32] As a fire extinguisher, it is sold under the trade mark "Pyrene" and as a dry cleaning agent it is sold under many trade names one of which is "Carbona." "Chlorasol" is a trade mark for a mixture of 25 per cent carbon tetrachloride and 75 per cent ethylene dichloride and is used as a fumigant. Some other trade names are Asordin, Benzinoform, Phoenipine, Spectral, Tetra, Tetracol, Tetraform and Katarine.[33]

Carbon tetrachloride, tetrachloromethane, CCL_4, is a colorless, non-inflammable liquid with a characteristic odor. It boils at 76.7° C., has a specific gravity of 1.589 at 25° C.; and has a refractive index of 1.4607 at 20° C. One cc. of carbon tetrachloride is soluble in about 2,000 cc. of water. It is miscible in all proportions with alcohol, benzene, chloroform, ether, petroleum ether, etc. While carbon tetrachloride is non-inflammable at ordinary temperatures, at elevated temperatures it will decompose with the formation of small quantities of hydrochloric acid and phosgene. Under ordinary conditions, when carbon tetrachloride is used to extinguish fires in relatively open spaces the concentrations of phosgene and hydrochloric acid produced are irritating but not very harmful, but in small enclosed spaces, such as in a vault, a closet, or small cellar room, especially where there is no simple exit. there is danger of sufficiently high concentrations of these toxic substances to be harmful.[34] The decomposition products of carbon tetrachloride have adequate lachrymatory warning properties.

a) Physiological Response

Carbon tetrachloride is an anesthetic. The systoms caused by carbon tetrachloride poisoning are irritation of the nose, eyes and throat, headaçhe, nausea, vomiting, abdominal pain, diarrhea, stupor deepening into coma, convulsions, weak pulse, fever, uremia and death. The safety limit for prevention of acute poisoning is given as 1,000 parts per million by the U. S. National Safety Council. The Retail Credit Co.[35] of Atlanta, Ga. regards the safety limit for acute intoxication as ranging from 1000-1600 parts per million. The safe limit for continuous exposure is regarded as 100 parts per million by Davis[36] and also by Smyth, Smyth and Carpenter.[37]

Carbon tetrachloride is lethal to guinea pigs in concentrations of the order of 2-2.5 per cent by volume for continuous durations of exposure of the order of 1 hour. A concentration of 4.8-6.3 per cent by volume of carbon tetrachloride vapor in air will kill most animals in a few minutes. Concentrations of 2.4 to 3.2 per cent by volume are dangerous to the life of animals for durations of exposure of from 30 to 60 minutes. The maximum concentration tolerated for 60 minutes without serious disturbances is in the range 0.4-0.6 per cent and the maximum concentration tolerated for several hours or for prolonged exposure with but slight symptoms is 0.16 per cent.

The least detectable odor of carbon tetrachloride vapor in air is 71.8 parts per million.[38,39]

Carbon tetrachloride is about twice as toxic as chloroform which itself is about 100 times as toxic as ethyl alcohol.[40]

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[32] Moller, J. Ind. Hyg., 15, 418 (1933).

[33] Sappington, Medicolegal Phases of Occupational Diseases. Chicago, 1939.

[34] Nuckolls, Nat. Bd. Fire Underwriters, Misc. Hazard, 2375 (1933).

[35] J. Am. Med. Assoc. 97, 48 (1934).

McConnell[41] states that carbon tetrachloride is more toxic than chloroform. Its narcotic effects are less marked but its effect on the liver, heart and kidneys is much more rapid.

THE ANALYTICAL CHEMISTRY OF INDUSTRIAL POISONS,
HAZARDS AND SOLVENTS

Chapter XVI Page 480

2. Ethyl Alcohol

Ethyl alcohol is universally used in industry as a solvent. It is a component of a vast number of mixtures and solutions of a pharmaceutical nature. It is a solvent for resins and many organic and inorganic chemicals. It is used in the manufacture of phroxylin and other plastics, the manufacture of vinegar, of rayon, of ethyl ether, of esters, acetic acid and many other organic chemicals. It is used as a diluent in shellac, in varnishes, lacquers, and enamels. It is used as a liquid fuel. It is a component of cosmetic and toilet preparations, antiseptics, and disinfectants. The production of synthetic drugs, dyestuffs, cleansers, lubricants, and a host of other materials and products requires the use of a large amount of this solvent.

Probably the most common point of contact of ethyl alcohol and man, is not in industrial applications but as the alcoholic beverages, whiskey, wine and beer.

Stringent government regulations cover the manufacture, use, and sale of ethyl alcohol in all forms. Alcohol not for beverage

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36 Davis, J. Am. Med. Assoc., 103, 961, (1934).
37 Smyth, Smyth and Carpenter, J. Ind. Hyg. Toxicol., 18, 277 (1936).
38 Sayers, Yant, Thomas and Berger, U. S. Pub. Health Service, Bull. No. 185, (1929).
39 Sayers, DallaValle and Yant, Ind. Eng. Chem. 26, 1251 (1934).
40 Waller, Lancet (1909) Vol. 2, p. 369.
41 McConnell, J. Am. Med. Assoc., 109, 762 (1937)

purposes is tax-free. However, such tax-free alcohol is either used under direct governmental supervision or, after being completely or specially denatured so as to render it unfit for beverage purposes, is used without direct supervision. The use of all alcohol, whether tax-paid, tax-free or specially or completely denatured must be accounted for by the use of records.

Ethyl alcohol, CH_3CH_2OH, is a colorless liquid with a pleasant odor and a burning taste. It boils at 78.5° C, and when distilled with water will form a constant minimum boiling point for the mixture of 78.15° C. consisting of 95.6 per cent of alcohol and 4.4 per cent of water. Its density is 0.7893 at 20° C. referred to water at 4°C. It has a refractive index of 1.361 at 20° C. Ethyl alcohol is designated as "alcohol", in contradistinction to all other alcohols which must be specifically named. Anhydrous ethyl alcohol is termed "absolute" alcohol.

Ethyl alcohol is miscible with water and ethyl ether in all proportions and, as its vast use in industry indicates, is capable of dissolving a great many substances. When ignited it burns in air with a pale blue, transparent flame with the formation of carbon dioxide and water. The vapor forms an explosive mixture with air.

a) Toxicity and Physiological Response

The intoxicating effect of alcoholic beverages became a matter of national importance a generation ago and the alcoholic liquor prohibition amendment was added to the Constitution of the United States in 1919, as Article XVIII. Its importance did not diminish with the succeeding years and Article XVIII was repealed by a subsequent amendment, Article XXI. The agent that produces the intoxicating effect of alcoholic beverages is ethyl alcohol. In the human body, the principal action of ethyl alcohol is that of a mental depressant, not a stimulant, as is commonly believed. In moderate doses, well-diluted alcohol stimulates the appetite, induces secretion of gastric juice and aids in the absorption of food. When injested repeatedly in stronger forms than mild alcoholic beverages, alcohol is an irritant to the mucous membrane lining of the stomach. When ethyl alcohol is taken to excess it is particularly toxic to the nervous system paralyzing the respiratory center and is a direct and principal cause of several kinds of mental disease. When inhaled it acts principally as a narcotic.

b) Detection

In order to detect the presence of alcohol vapor in air, the air should be passed through some trapping device containing water at a rate of about 20 liters per hour. This sample can then be transferred to a volumetric flask, made to volume with water washings of the bubbler and aliquots can be withdrawn for qualitative and quantitative estimation. Very small amounts of alcohol can be detected by means of the iodoform test and the ethyl benzoate test. (These two tests are outlined in this book on page 482.)

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3. American Standard: "Maximum Acceptable Concentration of Carbon Tetrachloride", American Standards Association. Reg. U. S. Patents Office, 1957.

4. Guide for Safety in the Chemical Laboratory. The General Safety Committee of the Manufacturing Chemists' Association, Inc., Washington, D. C. D. Van Nostrand Company, Inc., New York, 1954.

5. Product Information: "Acetylene Tetrabromide," The Dow Chemical Company; Midland, Michigan.