DEVELOPMENT OF A GPC ANALYSIS METHOD FOR
ESTANE IN LX-14

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MASTER

DEVELOPMENT DIVISION

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ABSTRACT

A High Speed Gel Permeation Chromatography (HSGPC) method was developed for the molecular weight parameter analysis of Estane as a minor component in LX-14 PBX formulations. Molecular parameters for Estane, so obtained, permitted the evaluation of various aging and accelerated aging treatments on the LX-14 samples.

Parameters evaluated were: Number average molecular weight, $\bar{M}_n$, weight average molecular weight, $\bar{M}_w$, and peak molecular weight, M_p , as well as the derived ratio, $\bar{M}_w/\bar{M}_n$, generally referred to as the molecular weight distribution index (MWD).

The method employed the Waters High Speed Gel Permeation Chromatograph (HSGPC) together with a Waters Model 440 UV detector. Molecular weight data obtained had a standard deviation of approximately 5%.

DISCUSSION

In the course of long-term compatibility studies of LX-14 samples it became apparent that changes in the mechanical properties of the PBX occurred which might be due to thermal degradation or other reactions of the Estane component in these samples. Since small changes in the molecular weight parameters of such a binder could result in significant losses in the strength of the PBX, molecular weight characterization of the Estane in LX-14 was of considerable interest.

To effect this demanding analysis, which requires precise molecular weight data of the polymer in a matrix of 95% HMX, the available Waters liquid chromatograph, Model ALC-100, was upgraded into a HSGPC. Six microstyragel columns, a Model UK6 injector, a Model 440 UV detector, and several smaller modifications were incorporated. Initial temperature control for the columns was not available and an internal standard method was developed and used to correct for ambient temperature fluctuations. Later, column temperature blocks were installed but use of the internal standard method was continued, as it helped to compensate for small variations in the solvent flow rate which could not be avoided.

The standard refractive index detector (RI) was found to be inapplicable for this work as its sensitivity is insufficient for the small samples which are required in order to avoid overloading of the columns(1,2). Such overloading results in serious distortions of the derived molecular weight parameters and negates the reliability of interpretations derived from them.

The ultraviolet detector (UV) on the other hand was found to be quite satisfactory for the Estane system since its emission source at 254 nm is within the range of high absorbance of the aromatic components of the polymer. It was thus possible to obtain good chromatograms, with little baseline noise and good shape reproducibility, at low polymer levels (5 μ g), such that sample loading was not a factor.

To obtain the required molecular weight parameters the recorder tracings of the chromatograms were photographically reduced to suitable size and were then read on a Grant comparator, which was interphased with a Wang calculator. The program employed was a modified version of one described by R. W. Ashcraft(3) and is reproduced in the Appendix.

The program incorporated a calibration curve which was developed from a least square fit of data from polystyrene calibration standards. The molecular weights were adjusted by use of the Q-value of 20 which has been published by Schrollenberger(4). This value was established at an Estane molecular weight of 41,000 and is strictly valid only at this value. At substantially larger or smaller molecular weights significant deviations from 20 are anticipated but corrections for such deviations were not made in the calculations, as these would require data which were not available or readily obtainable during the course of the present work.

The Wang program related retention distance on the recorder tracing of the UV detector output to molecular weight by means of an exponential function, in such a manner that a small variation in the retention distance on the chromatogram corresponded to a large change in the molecular weight. Therefore, minute changes in the retention distance, resulting from temperature fluctuations or flow variations, produced sizable errors in the molecular weight parameters and required a compensatory mechanism.

To correct for such fluctuations the trace of the RI detector was simultaneously recorded with the UV trace and the distance between the injection point and the peak of the HMX in the sample was measured on the RI trace. This information was then used to adjust the retention values of the UV trace in the manner described in the experimental section.

While the same HMX peak was also present on the UV trace it was too large to be on scale because of the high UV absorption of HMX and the high intensity setting which was required to observe the small proportion of Estane in the sample. Utilization of the UV trace for internal standardization is possible but would have required an exactly timed reduction in the sensitivity of the detector.

The molecular weight parameters obtained from the printout of the calculator were the number average molecular weight, $\bar{M}_n$, the weight average molecular weight, $\bar{M}_w$, the z-average molecular weight, $\bar{M}_z$, and derived quantities. The peak molecular weight, M_p , was also measured. The latter is not a true average but always appears between $\bar{M}_n$ and $\bar{M}_w$ and is useful in identifying a particular sample.

The averages were extremely sensitive to small variations in the shape of the chromatogram. In particular, the $\bar{M}_n$ was markedly affected by the shape of the curve at large retention distances (A in Fig. 1), especially the height of the curve from the baseline, while the $\bar{M}_w$ and $\bar{M}_z$ were

Fig. 1. Sample Chromatogram

strongly influenced by deviations at short retention distances, adjacent to the onset of the peak (B in Fig. 1). The assignment of the baseline was therefore of great significance and was the source of some arbitrariness in the measurements. The baseline assignments, however, were made a priori (see Experimental Section) and were therefore not subject to bias.

A problem with the analysis was posed by the presence of a small peak which is attributed to a minute impurity in the HMX and occurs at the low molecular weight tail of the Estane curve (C in Fig. 1). Because of this peak the lowest molecular weight components of the Estane molecular weight distribution could not be measured and an error was introduced in the results which was significant for the M_n 's, but not for the other averages. This error was greatest with the lower molecular weight samples.

A comparison of MWD's of high molecular weight and lower molecular weight samples is, therefore, not entirely clear cut because the MWD values of the low molecular weight samples were more substantially increased by the absence of contributions from the very low molecular weight components. It is expected that correction of this problem could be accomplished by multiple cycling of the sample through the GPC columns and the resulting complete resolution of the HMX and Estane peaks, but such a procedure would have increased the analysis time many-fold and was beyond the scope of the present work.

Tabulation of the results, covering 31 LX-14 analyses and 25 Estane controls and a preliminary interpretation relating to weapons components, is presented in a companion report(5). The standard deviation (σ) for the molecular weight parameters was usually near 5%.

EXPERIMENTAL

The analyses of LX-14 samples and of Estane 5702-F1 control samples were performed on a Waters ALC-100 liquid chromatograph which was equipped with a Model 6000 pump, a Model U6K high pressure injector, an R-400 differential refractometer and a Model 440 absorbance detector, operating at 254 nm. The pump was equipped with the modified pump heads supplied with the Model 6000A pump, and the 3-solvent manifold was also used.

Six microstyragel columns, supplied by Waters Associates, were used in series. They had nominal pore sizes of 100 Å, 500 Å, 10^3 Å, 10^4 Å, 10^5 Å, and 10^6 Å and were arranged in that order, with the sample entering the smallest pore size column first.

The columns were equipped with temperature blocks supplied by Waters through which fluid from a Forma Scientific constant temperature bath, Model 2095 was circulated. The nominal temperature of the bath was 25 C and control was generally within ± 0.1 C. The temperature in the columns was about 0.2 C higher in the last column and intermediate in the others, because of the frictional effect of the fine particles in the packing.

The output from the detectors was graphed on a Perkin-Elmer 1 mv dual pen recorder which was normally operated at a sensitivity of 10 mv and a chart speed of 5 mm/min.

The solvent used was tetrahydrofuran (THF) supplied by Burdick & Jackson Laboratories, Inc. It was unstabilized, distilled in glass, with a UV cutoff of less than 212 nm and a maximum water content of 0.03%. The solvent was deaerated just prior to use by means of vigorous magnetic stirring under vacuum until evolution of all bubbles was not observable for a period of five minutes. The solvent was then immediately transferred to the chromatograph and placed under a blanket of pure nitrogen. The solvent flow rate was 2.3 ml/min, nominal, and was found to vary less than 2% by occasional calibration. The pressure generated by the pump at this flow rate was about 6.9×10^6 Pa.

Sample solutions were prepared on a weight per volume basis (w/v) by dissolving approximately 0.5 g of sample in 100 ml of THF through gentle agitation of the mixture. Approximately 10 ml of the solution were then passed through a 1 μ Millipore filter and stored in a bottle capped by a Teflon Mininert Valve, supplied by the Precision Sampling Corporation. Normally 20 μ l of the solution were injected into the chromatograph for each analysis. The process of injection produced an instantaneous blip on the recorder traces of each detector, exactly defining the injection point.

The recorder tracings of the chromatograms were reduced photographically to a size acceptable to the Grant Comparator (less than 10 cm total value of the ordinate of the Estane peak) and were then read on the Grant. The reading procedure is somewhat complicated and is implicitly contained in the Wang program (see Appendix). Briefly, the injection points for both detectors were recorded (I and I' in Fig 1) and the distance to the HMX Peak (N in Fig. 1) on the RI trace was determined. This value was used to normalize the distances on the UV trace which were then converted into molecular weights by the program (T-factor). A constant distance correction factor (R-factor) was also used in the program to make small adjustments in the calibration subroutine of the program which would bring the molecular weights in line with measurements made on standard polystyrene samples, which were made from time to time.

The baseline was determined by the operator of the Grant Comparator by designating the value of the ordinate at the point at which the chromatogram just commenced (D in Fig. 1). This point was usually recognizable by a nearly imperceptible dip, the cause of which is not known. The evaluation of molecular weights on the chromatogram trace was abruptly terminated at a point just prior to the small HMX peak where the ordinate had its lowest value.

The position of the peak of the chromatogram (P in Fig. 1) was also determined by the Grant operator and was used directly in the program to calculate the peak molecular weight, M_p , (designated as MW (1) in the program). From the Grant ordinate readings made by the operator the program calculated the standard molecular weight parameters, $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, and the derived ratios $\bar{M}_w/\bar{M}_n$ (MWD), the Lowry Index, and $\bar{M}_z/\bar{M}_n$, which is

a more sensitive measurement of changes in the molecular weight distribution but which in this work was primarily used for diagnostic purposes. A sample printout is shown in the Appendix along with the program.

Usable chromatograms were only obtained under circumstances where the instrument conditions were essentially perfect. That is, that there were no bubbles of even minute size anywhere in the solvent train, including the pump heads, the lines, the detectors, and probably also the columns. Minute leaks in the valves or fittings could also not be tolerated. Conditions such as those enumerated produced chromatograms with wavy or drifting baselines and retention distances which did not agree with calibration.

CONCLUSIONS

The HSGPC method for the evaluation of the molecular weight parameters which was developed employing microstyrigel columns and the new Waters absorbance detector was found to be rapid and produced highly consistent results which were found to be useful in aging studies of LX-14 samples.

The method did not yield accurate absolute molecular weights or distributions because of the uncertainty of the Q-value of Estane and its probable dependence on molecular weight.

The internal standard method in conjunction with the attained temperature control in the columns permitted efficient utilization of the new microstyrigel columns in the rapid analysis mode. Further development work, however, is needed to shorten downtime of the instrument and reduce or eliminate factors which cause unusable analysis runs. More efficient and effective data processing techniques also need to be developed.

FUTURE AND RELATED WORK

The HSGPC method is capable of furnishing molecular weight parameters of polymers with an accuracy that matches much more time-consuming techniques, providing absolute calibrations can be carried out. An automatic membrane osmometer will supply such information and increase the applicability and effectiveness of the method.

The data processing method currently employed and described in this report is indirect and time consuming. Work is presently underway to develop a direct data acquisition procedure in which the detector output is directly processed by the Wang calculator, using a digital voltmeter, timer and a storage device. It is expected that this will result in greater reproducibility of data, lower analysis cost per sample and significant improvements in flexibility of analyses and in accuracy. More effective data processing will also be possible through addition of a device which will permit transfer of the detector output to a high speed digital computer.

For applications to polymers which do not absorb or only weakly in the ultraviolet, other highly sensitive and reliable detectors are being investigated.

REFERENCES

1. Yoshio Kato and Tsutomu Hashimoto, Solvent Dependence of Concentration Effect in Gel Permeation Chromatography, J. Polymer Science, Polymer Physics Edition, Vol. 12, p 813 (1974).
2. J. C. Moore, The Overload Effect in Gel Permeation Chromatography, "Gel Permeation Chromatography," Altgelt, Ed. Marcel Dekker, Inc. (1971).
3. R. W. Ashcraft, Data Reduction of GPC Spectra, MHSMP-75-40R (July - September 1975).
4. C. S. Schollenberger and K. Dinbergs, Thermoplastic Urethane Molecular Weight-Property Relations, J. Elastoplastics, Vol. 5, pp 223-250 (October 1973).
5. P. A. Foster and E. Kohn, LX-14 Aging Studies, MHSMP-76-5I, (October - December 1975).

APPENDIX

Following is a Wang printout of the reading of a chromatogram on the Grant comparator and the program on which it is based.

GPC SAMPLE NUMBER C-340 No: 55

Q FACTOR 20.00000

R FACTOR 1.01900

RT FACTOR 1.02325

MW(1) = 49541.68

BASELINE Y 11254

MN	MW	MZ	MWD	LOWRY	MZ/MN
20451.55	56134.65	110338.67	2.7447	1.3208	5.3951

0000	0408	MARK	#	0070	0002	0002	0140	0200	0200	
0001	0701	1		0071	0411	WR	0141	0112	0112	
0002	0412	WR A		0072	0405	0405	0142	0101	0101	
0003	0108	0108		0073	0015	0015	0143	0205	0205	
0004	0103	0103		0074	0013	0013	0144	0209	0209	
0005	0015	0015		0075	0007	0007	0145	0104	0104	
0006	0005	0005		0076	0704	4	0146	0206	0206	
0007	0212	0212		0077	0708	8	0147	0205	0205	
0008	0002	0002		0078	0712	*	0148	0002	0002	
0009	0101	0101		0079	0705	5	0149	0001	0001	
0010	0112	0112		0080	0606	EX	0150	0102	0102	
0011	0115	0115		0081	0603	DIV	0151	0413	END A	
0012	0005	0005		0082	0605	DOWN	0152	0411	WR	
0013	0209	0209		0083	0402	X DIR	0153	0800	0800	
0014	0205	0205		0084	0002	0002	0154	0015	0015	SR
0015	0002	0002		0085	0405	RE DIR	0155	0009	0009	SR
0016	0206	0206		0086	0002	0002	0156	0700	0	
0017	0214	0214		0087	0412	WR A	0157	0404	ST DIR	
0018	0115	0115		0088	0103	0103	0158	0201	0021	
0019	0200	0200		0089	0113	0113	0159	0405	RE DIR	
0020	0205	0205		0090	0207	0207	0160	0003	0003	
0021	0113	0113		0091	0002	0002	0161	0011	0011	SR
0022	0413	END A		0092	0014	0014	0162	0010	0010	SR
0023	0703	3		0093	0112	0112	0163	0012	0012	SR
0024	0700	0		0094	0212	0212	0164	0408	MARK	#
0025	0604	UP		0095	0207	0207	0165	0702	2	
0026	0408	MARK	#	0096	0109	0109	0166	0009	0009	SR
0027	0601	-		0097	0113	0113	0167	0012	0012	SR
0028	0412	WR A		0098	0102	0102	0168	0407	SEARCH	*
0029	0000	0000		0099	0413	END A	0169	0702	2	
0030	0413	END A		0100	0411	WR	0170	0408	MARK	#
0031	0701	1		0101	0305	0305	0171	0703	3	
0032	0601	-		0102	0015	0015	0172	0015	0015	SR
0033	0412	WR A		0103	0408	MARK	0173	0411	WR	
0034	0411	WR	SKIP	0104	0704	4	0174	1506	1506	
0035	0407	SEARCH	*	0105	0013	0013	0175	0412	WR A	
0036	0601	-		0106	0700	0	0176	0115	0115	
0037	0015	0015	SR	0107	0404	ST DIR	0177	0206	0206	
0038	0412	WR A		0108	0005	0005	0178	0413	END A	
0039	0004	0004		0109	0404	ST DIR	0179	0411	WR	
0040	0002	0002		0110	0006	0006	0180	1511	1511	
0041	0014	0014		0111	0404	ST DIR	0181	0412	WR A	
0042	0112	0112		0112	0007	0007	0182	0115	0115	
0043	0212	0212		0113	0404	ST DIR	0183	0100	0100	
0044	0207	0207		0114	0008	0008	0184	0413	END A	
0045	0109	0109		0115	0404	ST DIR	0185	0411	WR	
0046	0113	0113		0116	0009	0009	0186	1511	1511	
0047	0102	0102		0117	0007	0007	0187	0412	WR A	
0048	0413	END A		0118	0405	RE DIR	0188	0115	0115	
0049	0715	CLEAR		0119	0002	0002	0189	0307	0307	
0050	0515	STOP		0120	0602	X	0190	0413	END A	
0051	0404	ST DIR		0121	0605	DOWN	0191	0411	WR	
0052	0000	0000		0122	0011	0011	0192	1510	1510	
0053	0411	WR		0123	0008	0008	0193	0412	WR A	
0054	0405	0405		0124	0013	0013	0194	0115	0115	
0055	0015	0015	SR	0125	0409	GR 1	0195	0100	0100	
0056	0412	WR A		0126	0700	0	0196	0213	0213	
0057	0113	0113		0127	0404	ST DIR	0197	0413	END A	
0058	0002	0002		0128	0010	0010	0198	0411	WR	
0059	0014	0014		0129	0409	GR 1	0199	1509	1509	
0060	0112	0112		0130	0701	1	0200	0412	WR A	
0061	0212	0212		0131	0014	0014	0201	0209	0209	
0062	0207	0207		0132	0404	ST DIR	0202	0109	0109	
0063	0109	0109		0133	0004	0004	0203	0100	0100	
0064	0113	0113		0134	0404	ST DIR	0204	0113	0113	
0065	0102	0102		0135	0011	0011	0205	0001	0001	
0066	0413	END A		0136	0412	WR A	0206	0413	END A	
0067	0715	CLEAR		0137	0108	0108	0207	0411	WR	
0068	0515	STOP		0138	0110	0110	0208	1507	1507	
0069	0404	ST DIR		0139	0103	0103	0209	0412	WR A	

0210	0115	0115		0280	0404	ST DIR		0350	0700	0	
0211	0307	0307		0281	0004	0004		0351	0014	0014	SR
0212	0102	0102		0282	0409	GR 1		0352	0404	ST DIR	
0213	0009	0009		0283	0700	0		0353	0004	0004	
0214	0103	0103		0284	0014	0014	SR	0354	0409	GR 1	
0215	0115	0115		0285	0604	UP		0355	0700	0	
0216	0206	0206		0286	0409	GR 1		0356	0014	0014	SR
0217	0108	0108		0287	0700	0		0357	0604	UP	
0218	0102	0102		0288	0014	0014	SR	0358	0409	GR 1	
0219	0413	END A		0289	0606	EX		0359	0700	0	
0220	0415	RE Y		0290	0406	EX DIR		0360	0014	0014	SR
0221	0006	0006		0291	0004	0004		0361	0401	- DIR	
0222	0405	RE DIR		0292	0601	-		0362	0004	0004	
0223	0005	0005		0293	0401	- DIR		0363	0601	-	
0224	0603	DIV		0294	0004	0004		0364	0405	RE DIR	
0225	0605	DOWN		0295	0405	RE DIR		0365	0004	0004	
0226	0404	ST DIR		0296	0004	0004		0366	0603	DIV	
0227	0106	0016		0297	0606	EX		0367	0414	ST Y	
0228	0411	WR		0298	0603	DIV		0368	0003	0003	
0229	0702	0702		0299	0405	RE DIR		0369	0715	CLEAR	
0230	0415	RE Y		0300	0003	0003		0370	0515	STOP	
0231	0007	0007		0301	0600	+		0371	0400	+ DIR	
0232	0405	RE DIR		0302	0511	RETURN		0372	0003	0003	
0233	0006	0006		0303	0408	MARK		0373	0511	RETURN	
0234	0603	DIV		0304	0008	0008	SR	0374	0408	MARK	
0235	0605	DOWN		0305	0701	1		0375	0012	0012	SR
0236	0404	ST DIR		0306	0400	+ DIR		0376	0405	RE DIR	
0237	0107	0017		0307	0009	0009		0377	0013	0013	
0238	0411	WR		0308	0405	RE DIR		0378	0607	ABS	
0239	0002	0002		0309	0009	0009		0379	0404	ST DIR	
0240	0415	RE Y		0310	0412	WR A		0380	0201	0021	
0241	0008	0008		0311	0108	0108		0381	0405	RE DIR	
0242	0405	RE DIR		0312	0103	0103		0382	0012	0012	
0243	0007	0007		0313	0115	0115		0383	0011	0011	SR
0244	0603	DIV		0314	0100	0100		0384	0010	0010	SR
0245	0605	DOWN		0315	0300	0300		0385	0405	RE DIR	
0246	0404	ST DIR		0316	0102	0102		0386	0015	0015	
0247	0108	0018		0317	0413	END A		0387	0607	ABS	
0248	0411	WR		0318	0411	WR		0388	0404	ST DIR	
0249	0002	0002		0319	0200	0200		0389	0201	0021	
0250	0415	RE Y		0320	0412	WR A		0390	0405	RE DIR	
0251	0107	0017		0321	0103	0103		0391	0014	0014	
0252	0405	RE DIR		0322	0301	0301		0392	0011	0011	SR
0253	0106	0016		0323	0002	0002		0393	0010	0010	SR
0254	0603	DIV		0324	0102	0102		0394	0405	RE DIR	
0255	0605	DOWN		0325	0006	0006		0395	0107	0017	
0256	0411	WR		0326	0413	END A		0396	0607	ABS	
0257	0604	0604		0327	0405	RE DIR		0397	0404	ST DIR	
0258	0701	1		0328	0200	0020		0398	0201	0021	
0259	0601	-		0329	0411	WR		0399	0405	RE DIR	
0260	0605	DOWN		0330	0902	0902		0400	0106	0016	
0261	0612	SR	SR	0331	0511	RETURN		0401	0011	0011	SR
0262	0411	WR		0332	0408	MARK		0402	0010	0010	SR
0263	0604	0604		0333	0015	0015	SR	0403	0405	RE DIR	
0264	0415	RE Y		0334	0412	WR A		0404	0109	0019	
0265	0108	0018		0335	0103	0103		0405	0607	ABS	
0266	0405	RE DIR		0336	0108	0108		0406	0404	ST DIR	
0267	0106	0016		0337	0110	0110		0407	0201	0021	
0268	0603	DIV		0338	0413	END A		0408	0405	RE DIR	
0269	0605	DOWN		0339	0511	RETURN		0409	0108	0018	
0270	0411	WR		0340	0408	MARK		0410	0011	0011	SR
0271	0604	0604		0341	0014	0014	SR	0411	0010	0010	SR
0272	0015	0015	SR	0342	0412	WR A		0412	0405	RE DIR	
0273	0015	0015	SR	0343	0103	0103		0413	0004	0004	
0274	0515	STOP		0344	0102	0102		0414	0400	+ DIR	
0275	0408	MARK	#	0345	0413	END A		0415	0109	0019	
0276	0007	0007	SR	0346	0511	RETURN		0416	0405	RE DIR	
0277	0409	GR 1		0347	0408	MARK		0417	0109	0019	
0278	0700	0		0348	0013	0013	SR	0418	0404	ST DIR	
0279	0014	0014	SR	0349	0409	GR 1		0419	0011	0011	

0420	0701	1	
0421	0400	+ DIR	
0422	0003	0003	
0423	0014	0014	SR
0424	0511	RETURN	
0425	0408	MARK	#
0426	0010	0010	SR
0427	0415	RE Y	
0428	0201	0021	
0429	0405	RL DIR	
0430	0200	0020	
0431	0603	DIV	
0432	0606	EX	
0433	0400	+ DIR	
0434	0005	0005	
0435	0606	EX	
0436	0602	X	
0437	0606	EX	
0438	0400	+ DIR	
0439	0006	0006	
0440	0606	EX	
0441	0602	X	
0442	0606	EX	
0443	0400	+ DIR	
0444	0007	0007	
0445	0606	EX	
0446	0602	X	
0447	0606	EX	
0448	0400	+ DIR	
0449	0008	0008	
0450	0511	RETURN	
0451	0408	MARK	#
0452	0009	0009	SR
0453	0409	CR 1	
0454	0700	0	
0455	0404	ST DIR	
0456	0012	0012	
0457	0409	GR 1	
0458	0701	1	
0459	0014	0014	SR
0460	0404	ST DIR	
0461	0013	0013	
0462	0409	GR 1	
0463	0700	0	
0464	0404	ST DIR	
0465	0014	0014	
0466	0409	GR 1	
0467	0701	1	
0468	0014	0014	SR
0469	0404	ST DIR	
0470	0015	0015	
0471	0409	GR 1	
0472	0700	0	
0473	0404	ST DIR	
0474	0106	0016	
0475	0409	GR 1	
0476	0701	1	
0477	0014	0014	SR
0478	0404	ST DIR	
0479	0107	0017	
0480	0409	GR 1	
0481	0700	0	
0482	0404	ST DIR	
0483	0108	0018	
0484	0409	GR 1	
0485	0701	1	
0486	0404	ST DIR	
0487	0109	0019	
0488	0405	RE DIR	
0489	0004	0004	
0490	0401	- DIR	
0491	0103	0013	

0492	0401	- DIR	
0493	0105	0015	
0494	0401	- DIR	
0495	0107	0017	
0496	0401	- DIR	
0497	0109	0019	
0498	0701	1	
0499	0412	WR A	
0500	0703	3	
0501	0403	DIV DIR	
0502	0013	0013	
0503	0403	DIV DIR	
0504	0015	0015	
0505	0403	DIV DIR	
0506	0107	0017	
0507	0403	DIV DIR	
0508	0109	0019	
0509	0405	RE DIR	
0510	0010	0010	
0511	0401	- DIR	
0512	0102	0012	
0513	0401	- DIR	
0514	0104	0014	
0515	0401	- DIR	
0516	0106	0016	
0517	0415	RE Y	
0518	0108	0018	
0519	0401	- DIR	
0520	0108	0018	
0521	0414	ST Y	
0522	0010	0010	
0523	0405	RE DIR	
0524	0108	0018	
0525	0403	DIV DIR	
0526	0102	0012	
0527	0403	DIV DIR	
0528	0104	0014	
0529	0403	DIV DIR	
0530	0106	0016	
0531	0403	DIV DIR	
0532	0108	0018	
0533	0405	RE DIR	
0534	0003	0003	
0535	0400	+ DIR	
0536	0102	0012	
0537	0400	+ DIR	
0538	0104	0014	
0539	0400	+ DIR	
0540	0106	0016	
0541	0400	+ DIR	
0542	0108	0018	
0543	0405	RE DIR	
0544	0002	0002	
0545	0402	X DIR	
0546	0102	0012	
0547	0402	X DIR	
0548	0104	0014	
0549	0402	X DIR	
0550	0106	0016	
0551	0402	X DIR	
0552	0108	0018	
0553	0511	RETURN	
0554	0408	MARK	#
0555	0011	0011	SR
0556	0604	UP	
0557	0704	4	
0558	0702	2	
0559	0601	-	
0560	0414	ST Y	
0561	0202	0022	
0562	0712	.	
0563	0703	3	

0564	0703	3	
0565	0707	7	
0566	0703	3	
0567	0706	6	
0568	0706	6	
0569	0412	WR A	
0570	0406	EX DIR	
0571	0602	X	
0572	0712	.	
0573	0708	8	
0574	0701	1	
0575	0704	4	
0576	0706	6	
0577	0707	7	
0578	0702	2	
0579	0412	WR A	
0580	0405	RE DIR	
0581	0601	-	
0582	0405	RE DIR	
0583	0202	0022	
0584	0602	X	
0585	0712	.	
0586	0701	1	
0587	0700	0	
0588	0701	1	
0589	0702	2	
0590	0702	2	
0591	0702	2	
0592	0412	WR A	
0593	0403	DIV DIR	
0594	0601	-	
0595	0405	RE DIR	
0596	0202	0022	
0597	0602	X	
0598	0712	.	
0599	0705	5	
0600	0709	9	
0601	0702	2	
0602	0702	2	
0603	0706	6	
0604	0412	WR A	
0605	0402	X DIR	
0606	0600	+	
0607	0405	RE DIR	
0608	0202	0022	
0609	0602	X	
0610	0712	.	
0611	0701	1	
0612	0702	2	
0613	0708	8	
0614	0706	6	
0615	0701	1	
0616	0706	6	
0617	0601	-	
0618	0405	RE DIR	
0619	0202	0022	
0620	0602	X	
0621	0701	1	
0622	0712	.	
0623	0708	8	
0624	0709	9	
0625	0701	1	
0626	0600	+	
0627	0605	DOWN	
0628	0613	10**X	
0629	0415	RE Y	
0630	0000	0000	
0631	0602	X	
0632	0605	DOWN	
0633	0404	ST DIR	
0634	0200	0020	
0635	0511	RETURN	
0636	0512	END	